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Life-cycle assessment, techno-economic analysis, and statistical modeling of bio-based materials and processes

by

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Program of Study Committee:
Kurt Rosentrater, Major Professor
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DEDICATION

I would like to dedicate this thesis to my mother Kristie, my father Matthew, and my grandparents Daryle and Linda Johnson, without whose unconditional moral and financial support I would not have been able to complete this work. Additionally, I would like to dedicate this thesis to Shaowei Ding, whose unconditional support and friendship has helped me accomplish my seemingly impossible goals.

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ABSTRACT

Mathematical and statistical modeling has been used extensively in fields relating to bio-renewables and biological systems. Modeling of this nature helps predict a variety of effects, such as environmental and economic impacts, that are incurred during the manufacturing of various bio-based products. Typical modeling methodologies include: techno-economic analysis (TEA); life-cycle impact assessment (LCIA); and statistical correlation matrix analysis. The use of these methodologies can potentially be harnessed to assess the environmental, economic, and indirect impacts related to the overall stages of a product's cradle-to-grave life cycle, which includes the extraction of raw materials to pre-processing, fabrication, transportation to consumer, and end-of-life treatment. Therefore, TEAs and LCAs can project the outlook of these impact parameters and highlight which unit operation(s) produce the largest impact throughout the entire life cycle. Using these projections, producers may potentially change their materials, fabrication methods, or any production parameter to round their operation to fit the needs, standards, and constraints of their environment.

This thesis is comprised of three separate research endeavors. The first study focused on a TEA of a hypothetical commercial conversion system which converts chicken blood to bio-based flocculant. A TEA was utilized to test the economic viability of commercializing the conversion process which was analytically successful during lab based scale. The study revealed that waste water surcharges, relative to specific pollutant characteristics (BOD, COD, TSS, and NH3) found prevalent in chicken blood, were shown to have an especially high economic impact on the overall process. Additionally, the overall results determined that the hypothesized conversion plant would be highly economic feasible.

The second study utilized both TEA and LCA methodology to model the processing and overall cost(s) of poly(lactic acid) (PLA) composite production for both in-organic and organic filler material, which was compared over three product part weights and five end of life treatment options. The analysis discovered a high amount of variance in economic and environmental impacts produced, which resulted from the inclusion of organic or inorganic filler, different product part weight, and dissimilar end of life treatment selections. The inclusion of inorganic filler(s) (glass and talc) were shown to produce the largest volume of environmental burden, while organic filler(s) (wood, rice husks, and DDGS) were shown to maintain the least amount of environmental burden and economic impact. Therefore, it was suggested that when paired with PLA composite production organic fillers should be utilized over inorganic substitutes.

The third study utilized non-linear growth analysis and a linear correlation coefficient matrix to analyze and compare corn growth effects when three different nitrogen applications (low, medium, and high) and three dissimilar rotation applications (Corn-Corn (C-C), Corn-Soybean (C-S), and Corn-Soybean-Grass-Legume (C-S-G-L)) were applied. This study was focused as a continuation of a previous research endeavor (Riedell, 2011) which analyzed the same data by different methodologies. The non-linear growth modeling was shown to confirm the data suggested in the previous study, which documented significant growth variances due to interactions between rotation treatment and nitrogen application under the C-C and C-S-G-L rotations. It was speculated that the inclusion (or lack of inclusion) of legumes with in rotation treatment played a significant role in how the corn grew the following year. The linear correlation mapping highlighted interesting interactions between soil nutrient elements (NO3 and P) and grain yield and starch content, this was previously un-documented.

CHAPTER I:

GENERAL INTRODUCTION AND LITERATURE REVIEW

General Introduction

With the progression of energy initiatives to sequester the future oil demand of the U. S., an abundant amount of pathways for development of applied bio-renewable resources have become incentivized (Schell et al., 2008). These quick advances have produced a new demand for bio-based resources that can sustainably fit the needs of our expanding population. Due to its overwhelming production of bio-renewable material, The U. S. agriculture industry has consequentially become an integrated component of many bio-renewable and bio-based products and applications (Lin et al., 2006). Common bio-renewable manufacturing processes include (but are not limited to): production of agricultural bio-char (McHenry et al., 2009); conversion of feedstock into bio-ethanol (Sukumaran et al., 2009; Wong et al., 2014); the production of bio-oil via fast pyrolysis (Zhang et al., 2013). The rapid expansion of these relatively new processes has in-turn created concerns relating to the environmental, economic, and sustainability implications resulting from the utilization of U. S. agriculture supply. A prime example, the “food vs. fuel” argument, insinuated that producing bio-ethanol using corn produced in the U. S. will lead to water and food supply shortages due to the unsustainable increase in corn production and the indirect effects associated (i. e. depletion of feed for meat production; depletion of corn based food; depletion of water due to irrigation, etc.) (Laursen, 2007). To investigate these concerns, many government, academic, and commercial researcher undertakings have utilized a variety of different mathematical and statistically based tools, which project the environmental and economic responses of manufacturing bio-based products (Ross et. al, 2002). Typical modeling methodologies include: techno-economic analysis (TEA); life-cycle assessment (LCA); and statistical correlation matrix analysis. The use of these methodologies can potentially be harnessed to assess the environmental, economic, and indirect impacts obtained from a product's cradle-to-grave life cycle, i. e., including extraction of raw materials to pre-processing, fabrication, transportation to consumer, and end-of-life treatment (Ross et al., 2002). A correlation matrix is used to investigate the reliance between multiple data set variables which are affected during the same time period and exposed to the same environmental conditions. Through rigorous modeling efforts, the use of these tools has been shown, over numerous examples, to successfully impact and provide benefit to the agriculture and bio-renewables industries (Ning et al., 2013).

Techno-economic analysis (TEA) may be characterized as a systematic tool which is utilized to analyze the economic viability, opportunities, and negative economic effects of manufacturing processes, by accounting for the overall variable, capital, and fixed costs (Simba et al., 2012). The utilization of TEAs have provided considerable benefit to the bio renewables industry; with the wide array of compatible bio-based materials, TEAs have played an integral part in determining which materials provide the greatest economic incentives for a particular product or process. Examples of bio-renewable processes where TEAs have been utilized include: the production of algae biodiesel (Nagarajan et al., 2012); production of extruded aquafeed (Ozoh et al., 2015); production of biofuel based on bio-oil gasification (Li et al; 2015).

Life-cycle assessment (LCA) is defined as a systematic approach to quantify the environmental consequences of a product or procedure; a LCA accomplishes this by quantifying energy, materials, and waste streams released into the environment through all stages of a products life cycle, i.e. cradle-to-grave (Roy et al., 2009; Walker et al., 2011; Corominas et al., 2013). Since the production of bio-renewable materials relies heavily on the acquisition of organic, usually plant based, resources, careless extraction of raw materials can pose heavy environmental burden and disruption on sensitive ecosystems (Ross et al., 2002). Further, many indirect effects of ecosystem manipulation are generally hard to predict. Therefore, the use of LCA as a prediction tool is widely applied by the bio-renewables industry in effort to reduce negative environmental effects of manufacturing products. Cases of applied LCAs include: conversion of lignocellulosic biomass into bio-based jet fuel (biojet) (Agusdinata et al., 2011); production of bio-based polymer composites (La Rosa et al., 2014); bio-ethanol production using straw derived substrates (Gabrielle and Gagnair, 2007).

Correlation matrix analysis is a statistically based tool used to analyze the interaction strength of multiple variables simultaneously. Although the use of this tool is widely applied in various fields of genetics (Kim et al., 2011), correlation matrixes have been applied to bio-renewable products and biological systems as well. Correlation analysis has been shown to be beneficial in many areas related to biological growth and soil enzyme activity. Applied instances relative to bio-renewables include: relationships between enzyme activity and microbial growth in soil (Frankenberger and Dick, 1983); drought monitoring and corn yield estimation (Unganai and Kogan, 1998); effects of wastewater irrigation on corn and sorghum plants (Al-Jaloud et al., 1995).

Through the methodologies described above, these research endeavors have produced a positive impact on the bio-renewable industry. The viability of utilizing chicken blood for synthesis of bio-based flocculant was determined, and the possibility of other renewable chicken blood derived products was highlighted. A detailed comparison of PLA composites produced with different manufacturing parameters was shown to produce unexpected, and previously undocumented, results, which may lead to the inclusion of more bio-based materials in commercialized PLA composite production. Lastly, the correlation matrix analysis revealed interactions between soil nutrient elements (N, P, and K) and growth characteristics (grain yield, grain starch content, and plant dry weight).

Literature Review

Chicken Blood Flocculant

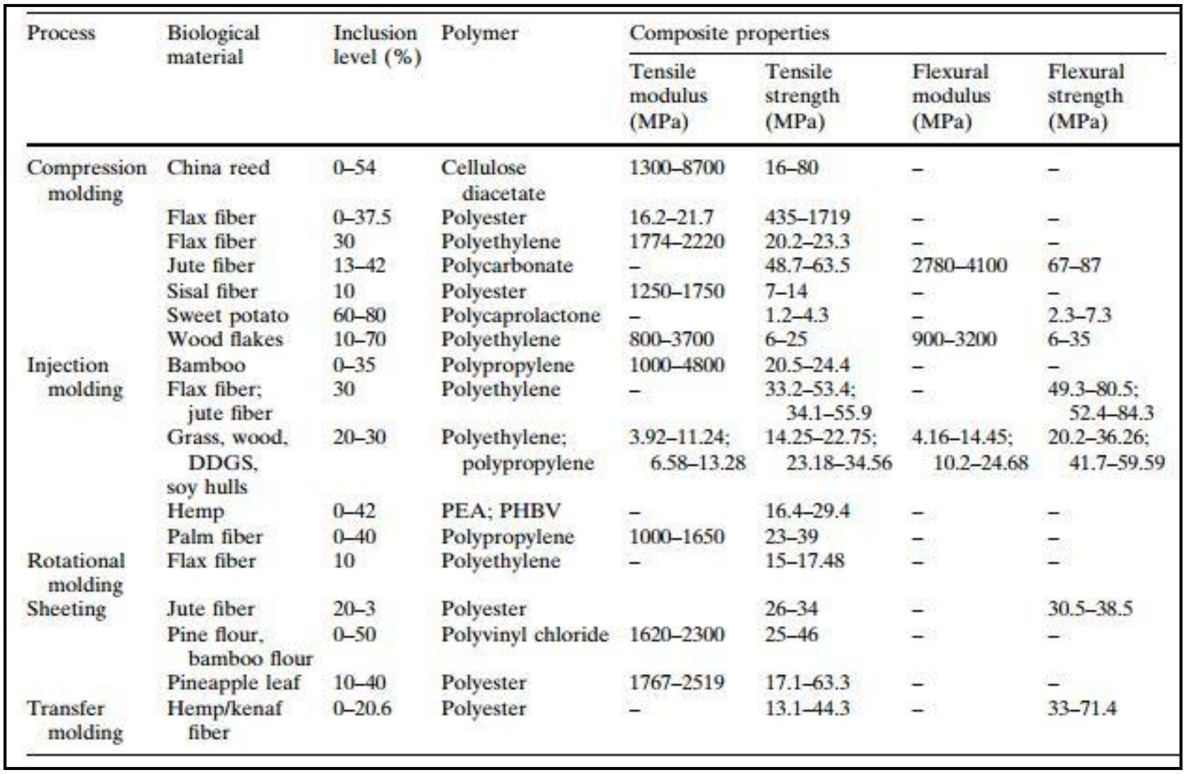
Each year nine billion chickens are processed within the U.S. (USDA, 2011). When slaughtered, chickens release 4.2% of their total body weight as drainable blood (CKB) (Carawan et al., 1979). In many poultry slaughterhouses across the nation CKB is only partially utilized and sold to rendering plants, and the remaining, blood serum, is placed in the wastewater stream, which leads to significant cleanup costs (Del Nery, 2007). With the bio-renewable movement emerging, new eco-friendly ways to utilize CKB may provide environmental benefit by sequestering pollutant characteristics of wastewater; it may also provide a possible source of income for chicken processing plants. It has been demonstrated that CKB maintains specific properties and compatibility as a renewable flocculant. To specify, in many studies flocculation and coagulation can be considered synonymous, as the process may be one in the same for the relative application. For this study the nomenclature of flocculant is utilized since the application of the product is mainly utilized to organize suspended solids into clumps, or flocs, of mass.

The CKB hemoglobin protein (hb), embedded in CKB red blood cells, has produced significant flocculant activity (Piazza et al., 2011). CKB flocculation performance has been investigated by viewing the influence CKB posed on the rate of settling of fine clay (kaolin) particles (Piazza et al., 2011). To quantify the efficiency of CKB flocculation it was tested against anionic polyacrylamide (PAM), a commonly used flocculant today, both varying in concentrations between experiments (Piazza et al., 2011). CKB fraction concentrations of up to 3 g/L were tested for flocculant activity, with and without 0.2 mM calcium chloride. Calcium ions are required for PAM flocculation and create an electromagnetic bridge between negatively charged particles (Piazza et al., 2011). It was shown that at pH 5.5 buffer there was significant flocculant activity in small concentrations of CKB (>0.12 g/L) (Piazza et al., 2011). To achieve a pH buffer of 5.5 inexpensive acids were utilized; citric acid was shown to reduce the hydrogen ion concentration by 100-fold and produce complete sedimentation after a five hour period (Piazza et al., 2011). To fully understand the applicability of CKB flocculant an overview of the economic aspects must be considered. In a parallel study (Piazza, et al. 2011), a preliminary economic analysis was performed on production costs and resource and environmental impacts. Due to a much lower unit cost ($0.075/lb), sulfuric acid is the preferred pH treatment acid (Piazza et al., 2011). Additionally, there is economic benefit to removing CKB from the wastewater stream by lowering the biological oxygen demand and cleanup costs (Piazza et al., 2011). Due to storage efficiency spray dried flocculant is proposed as a marketable material (Piazza et al., 2011). The highest costs of CKB flocculant production are confounded in: facility overhead, labor, utilities, and sulfuric acid. Capital costs related to dehydrating the CKB posed relatively high facility charges. It is projected that the cost of flocculant production will be $0.77 per pound (Piazza et al., 2011). After consideration of BOD removal, a total net cost of production is suggested at $0.33 per pound (Piazza et al., 2011). Compared to PAM, $1.20 per pound, CKB is effectively active at a 2:1 pound ratio, yielding a renewed CKB production cost of $0.66 per pound (Piazza et al., 2011). At half the cost of PAM, CKB may have a great economical/environmental effect in the poultry processing industry.

Bio-based Plastic and Poly(lactic acid)

Currently, there is still much ambiguity as to what defines a bio-based plastic. The International Union of Pure and Applied Chemistry (IUPAC, 2009) defines bio-based plastics as "Bio-based polymer derived from the biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow". Many industries consider bio-based plastics as plastics produced from biological sources, but bio-degradability is also a factor that shapes the definition. Almost all bio-based plastics can be considered bio-degradable under aerobic, or anaerobic, microbial conditions (Europe Plastics, 2008). Bio-plastics and bio-degradability do not always go hand in hand; many bio-based plastics are considered non-bio-degradable by maintaining a particularly slow degradation process (Europe Plastics, 2008). Alternatively, many chemically synthesized plastics may be bio-degraded, but chemical based plastics do fit the definition of a bio-based plastic (Europe Plastics, 2008). To compensate for the large array of applications bio-based plastics are applied to, many feedstocks are utilized and chosen depending on a variety of different factors. Feedstock compatibility is based on a number of dynamics including: shape, form, quality, supply, cost, physical properties, and machinability of raw feedstock materials (Rosentrater et al., 2006). Table 1 lays out a detailed overview of many feedstocks bases for bio-based plastic production. These materials include plant fibers, cellulosic derivatives, and bio-based by-products procured from other bio-based applications. Bio-based plastic materials are not limited to only plant feedstocks, PLA and PHB plastic granules are acquired from cultivation of micro-bacteria such as Lactobacillus, or Sporolactobacillus laevolactius, and Alcaligenes eutrophus, or Bacillus subtilis respectively (Abel et al., 1998).

Table 1. Feedstock Materials and Properties (Rosentrater, 2006**)**



Process	Biological material	Inclusion level (%)	Polymer	Composite properties			
				Tensile modulus (MPa)	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)
Compression molding	China reed	0–54	Cellulose diacetate	1300–8700	16–80	–	–
	Flax fiber	0–37.5	Polyester	16.2–21.7	435–1719	–	–
	Flax fiber	30	Polyethylene	1774–2220	20.2–23.3	–	–
	Jute fiber	13–42	Polycarbonate	–	48.7–63.5	2780–4100	67–87
	Sisal fiber	10	Polyester	1250–1750	7–14	–	–
	Sweet potato	60–80	Polycaprolactone	–	1.2–4.3	–	2.3–7.3
	Wood flakes	10–70	Polyethylene	800–3700	6–25	900–3200	6–35
Injection molding	Bamboo	0–35	Polypropylene	1000–4800	20.5–24.4	–	–
	Flax fiber; jute fiber	30	Polyethylene	–	33.2–53.4; 34.1–55.9	–	49.3–80.5; 52.4–84.3
	Grass, wood, DDGS, soy hulls	20–30	Polyethylene; polypropylene	3.92–11.24; 6.58–13.28	14.25–22.75; 23.18–34.56	4.16–14.45; 10.2–24.68	20.2–36.26; 41.7–59.59
	Hemp	0–42	PEA; PHBV	–	16.4–29.4	–	–
	Palm fiber	0–40	Polypropylene	1000–1650	23–39	–	–
Rotational molding	Flax fiber	10	Polyethylene	–	15–17.48	–	–
Sheeting	Jute fiber	20–3	Polyester		26–34	–	30.5–38.5
	Pine flour, bamboo flour	0–50	Polyvinyl chloride	1620–2300	25–46	–	–
	Pineapple leaf	10–40	Polyester	1767–2519	17.1–63.3	–	–
Transfer molding	Hemp/kenaf fiber	0–20.6	Polyester	–	13.1–44.3	–	33–71.4

PLA is a favorable bio-based plastic in the foreseeable future. PLA maintains a composition similar to petro-based plastics such as polypropylene and oil synthesized polyethylene. PLA has garnered much attention due to the ability to process granules through existing manufacturing infrastructure. Thus, eliminating the need for new equipment capital costs. Materials fabricated form PLA include: rigid packaging, cold drink cups, apparel, screws, medical equipment, and pharmaceutical capsules (Auras et al., 2010). PLA is formed directly from a condensation polymerization reaction using lactic acid. Figure 3 gives and in-depth look at the condensation polymerization reaction.

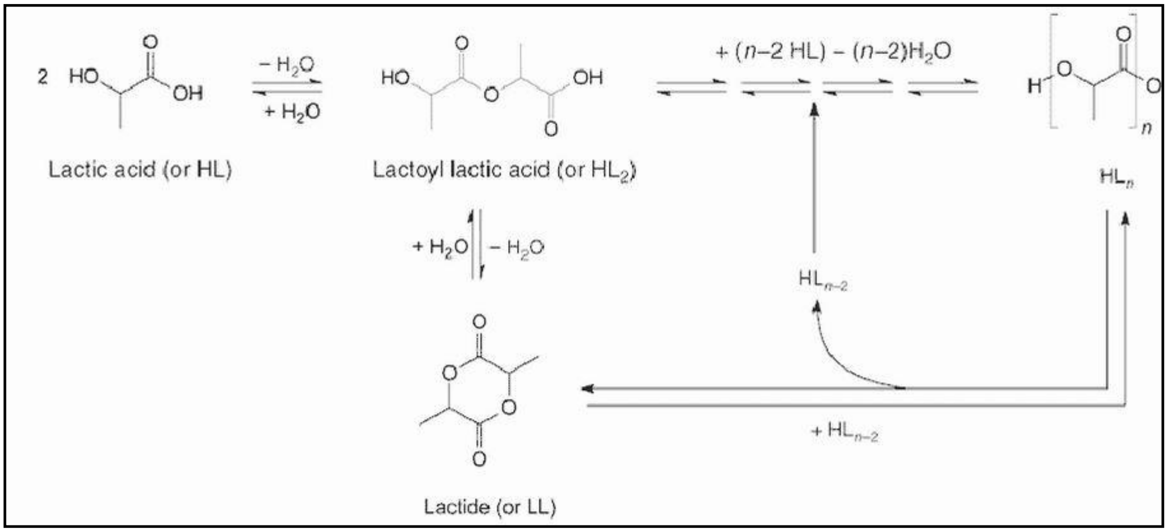


Figure 3. Lactic acid condensation reactions: lactic acid and lactide (Auras et al., 2010)

Lactic acid is obtained by fermenting sugar substrates using sugar-starch rich bio-mass. Examples include corn, tapioca, sugar cane, and sweet potato. Under anaerobic conditions, lactic acid producing microbes, such as Lactobacillus, convert carbohydrates into lactic acid (Auras et al., 2010). Figure 5 shows a detailed step by step process of how lactic acid is produced through fermentation.

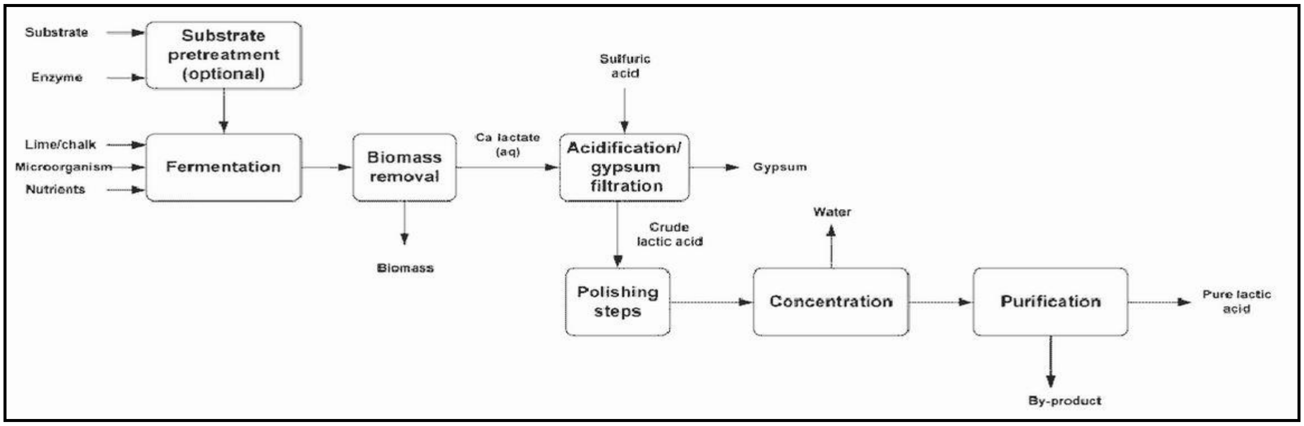


Figure 5. Fermentation to Lactic Acid Flow Diagram (Auras et al., 2010)

The current commercialized method is to produce lactide instead of lactic acid. Lactide is shown in figure 3 as a cyclic dimer of lactic acid (Auras et al., 2010). Production of lactide includes de-polymerization of PLA chains in restrained pressure (Auras et al., 2010). After purification, lactide may be used for PLA. This is the favorable method due to the reduced unit operations in order to produce a PLA ready polymer. PLA sequesters, on average, 2.5 kg CO2 per kg of PLA produced in the United States (Erwin et al., 2003). Also, it is shown that fossil energy use to produce PLA is 7 MJ/kg or PLA. PLA is a completely bio-degradable resource and can be recycled into same product life cycles with little refinement (Erwin et al., 2003). Life cycle analyses show many economic (carbon credits), environmental, and emission reducing capabilities to which fossil-based plastics fail to encompass (Erwin et al., 2003). Due to highly sustainable characteristics, full recycle potential, and current commercial proficiency PLA is widely considered to be the bio-based plastic of the future.

Rotation and Fertilization Treatment on Corn Growth

American corn production has securely fastened its roots into many dynamic applications and has been constantly re-invented to fit into today’s society. Corn has not only become a main diet source for many Americans, but it has also crept into many diets as an artificial sweetener, high fructose corn syrup. Many food processors have begun utilizing pure cane sugar over high fructose corn syrup do to availability and economic incentives (Buck, 2001). Substantial corn production areas have used corn as a source for animal feed. In 2006, 30% of the corn produced in Iowa was fed to the local feed stock. During the 2006-2008 periods, the Iowa State University Animal Industry reported that 70% of the corn produced in Iowa was exported out of state to be processed into ethanol, pet/animal feed, and artificial sweeteners (Pelletier, 2009). In recent years, corn has gained the national spotlight as the main bio-mass crop to be processed into bio-ethanol. Although the overall effectiveness and energetic returns are widely debated, the production of fuel grade ethanol from corn cannot be denied. Currently, the U.S. produces 2.81 billion gallons of ethanol each year (Pimentel, 2005). Consequentially, corn production in the United States has proven to be a vital component for many renewable energy pathways (bio-gas, bio-char, and bio-oil). To keep up with the increasing demand, researchers continually examine new, and more efficient, crop growth methods, many abstract ideas are examined. One method, free living bacteria inclusion, has been shown to promote plant growth when plotted parallel with crops. PGPR (Rhizobacteria) may form symbiotic relationships with plants and enables prevention of deleterious effects that a phytophathogenic organism can perform. Straight forward promotion of plant growth by PGPR is produced by the facilitation of nutrients from the environment which fortifies a plant’s nutrient pathway (Glick, 1994). Further, breakthroughs within molecular genetics have pushed the limits of annual crop yields within the last 10 to 20 years. Molecular genetic studies have produced hybrid crops which promote genes enhancing: yield, pest tolerance, heat, and expression in heterosis (Hallauer, 2008).

From 2001-2008 the average U.S. corn yield equaled 146 bushels/acre (2001) to 181 bushels/acre (2004) (Hallauer, 2008). Researchers are now predicting a jump to 300 bushels/acre within the next 20 years (Hallauer, 2008). The value of growing crops in planned sequences has been revealed by low yields due to one-crop systems over same land spaces (Curl, 1963). During a 1984 study, the Crop Science Society of America (Hauck, 1984) found legumes planted in rotation were able to re-furnish the soil with a temporary supply of nitrogen. The study also suggests there is no amount of nitrogen fertilizer able to ameliorate with the 5 to 10% yield disadvantage produced using a back to back corn rotation (Hauck, 1984). A 1985 study (Dick and Van Doren, 1985) suggested a negative response to no-tillage due to large decreases in yield (-880 kg/ha) obtained from continuous corn rotation. Even with a relatively expensive environmental impact, nitrogen applications have proven useful for many farmers intending to keep a consistent back to back corn planting cycle. Nitrogen has been shown to have a great overall impact when there is an absence of crop rotation (Hallauer, 2008). Also, studies have concluded that the timing of nitrogen application, and when tillage has been applied to the soil, can play a significant role in the amount of corn yield produced in a year (Vetsch, 2004). Where there is an uncertainty in yield response, farmers tend to add excess nitrogen to insure there are no nitrogen deficiencies and achieve yield increases in years with lower than normal yield efficiencies (Bock, 1984). To increase the overall nitrogen concentration in the soil, from year to year, farmers decrease the acreage and frequency of crops that receive nitrogen fertilizer in the crop rotation, as well as maintaining crop cover on over the land as long as possible (Olsen, 1970). Researchers have observed corn as an expensive nitrogen utilizer; high nitrogen root uptake and minimal nitrogen responses were shown in systems over a 9 year period due to low soil nitrogen capacity from corn-corn rotations (Zielke, 1986).

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CHAPTER II:

OBJECTIVES AND HYPOTHESES

The overall objective of the research undertakings provided in this thesis was to apply mathematical and statistical techniques on bio-based and/or bio-renewable product manufacturing. More specifically, the specific research objectives were:

1. To determine the viability of commercializing the conversion of chicken blood to bio-based flocculant, and determine which unit operations incur the largest economic impact by utilizing TEA methodology;
2. To compare the economic and environmental impact of producing PLA composites with different bio-based and synthetic fillers, end-of-life treatments, and part sizes by utilizing TEA and LCA methodology;
3. To further investigate interactions between soil element chemistry and corn growth characteristics due to different nitrogen application (low, medium, and high) and rotation treatment (C-C, C-S, and C-S-G-L) documented in a previous research study (Riedell et. al, 2011), and carry out the analysis using new statistical methodology, i.e. correlation matrix analysis and non-linear growth modeling.

In addition to the main objectives, the hypotheses are provided as well:

1. H_A: The chicken blood-to-flocculant preliminary commercial projection is shown to be economically feasible; the waste water surcharge will make up a majority of the associated variable cost;

2. H_A: Fabrication of PLA composites utilizing bio-based fillers will incur a lower economic and environmental impact compared to impacts associated with composites filled with petro-based fillers;
3. H_A: Nitrogen application and rotation treatment will have significant interactions in corn growth characteristics; soil nutrient elements (N, P, and K) will have significant interactions with yield and grain starch content.

Thesis Organization

Chapters 2, 3, and 4 correspond to the research goals outlined above. Specifically, Chapter 2 details the TEA analyzing the viability of converting chicken blood to bio-based flocculant. Chapter 3 is a TEA and LCA comparing the economic and environmental impact of PLA composites filled with synthetic and bio-based fillers. Chapter 4 is a statistical correlation and non-linear growth model of corn growth and soil nutrient elements, where interactions are analyzed due to different nitrogen applications and crop rotation treatments. Lastly, Chapter 4 summarizes all conclusions achieved through the research and plans for future work in mathematical and statistical modeling of biological systems.

CHAPTER III:

TECHNO-ECONOMIC ANALYSIS OF CHICKEN BLOOD-TO-FLOCCULANT PRODUCTION

Abstract

This research paper provides a Techno-Economic Analysis (TEA) of a theoretical chicken blood-to-bio-based flocculant conversion plant. Our hypothesis speculates that converting chicken blood to flocculant will produce a high profit margin due to the inexpensive and renewable inflow of chicken blood. To test our hypothesis, we modeled a base-line production scheme using TEA methodology. A 92,000 gallon per day chicken blood processing scenario was developed: the scenario utilized a centrifugation and ultrasonic processing pairing to isolate the erythrocyte hemoglobin embedded within the red blood cells. This research has revealed that construction expenditures and spray dryers have the highest economic impact on capital costs at 39% and 33% of overall costs, respectively. Further, sewage surcharge, materials (isotonic saline, EDTA, lab supplies, etc.), and utilities (tippage, gas, electricity,etc.) were shown to have the greatest impact on variable costs at 49%, 21%, and 20% overall, respectively. The modeling effort resulted in bio-based flocculant production rates of 10,400,000 kg of dry flocculant per year. Capital cost for this scenario amounted to approximately $4.1 million. Flocculant product value estimates are $1.00 per kg of flocculant. The projected annual revenue of this scenario was $2.34 million per year. Our research concluded that major economic incentives for production of facilities similar to this scenario are plausible and should be further explored. While competitive, calculated bio-based flocculant costs are preliminary, therefore, further research is advised to analyze the impact of raw material properties and production constraints on the overall yield of flocculant product.

Introduction

Chicken blood is known to be the main pollutant contributor in poultry slaughter waste streams (EPA, 1975). With the absence of pre-treatment or removal of chicken blood, slaughter houses face expensive sewage surcharge rates and environmental damage fines. (Mercado et al., 1995). To help sequester surcharges produced from blood comprised waste streams, many processors have been known to spray dry excess blood and sell it off as blood meal animal feed (Wisman et al,. 1957). Alternatively, many research endeavors have focused on pre-treatment methods which reduce poultry slaughter waste water pollutant loads, common pollutant characteristics include: biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), and ammonia (NH3). Pre-treatment research has analyzed, among many, up-flow anaerobic sludge blanket (UASB) reactors (Chavez et al., 2005), anaerobic filters (Ruiz et al., 1997), and anaerobic batch reactors (Masse et al., 2001). Although pre-treatment has been shown to be an effective method, over 92% COD removed and between 80%-96% TSS removed (Ruiz et al., 1997), many processors may opt out due to little or no economic incentive. In turn, there has been increased commercial interest in utilization of recovered chicken blood constituents. One example includes production of dried sludge from ferric sulfate poultry slaughter waste water treatment, which can be used for steam generation (Jayathilakan et al., 2012). Another includes recovery of bio-based flocculant from poultry slaughter blood (Piazza et al., 2011; Garcia et al., 2014). A 2014 study (Garcia, 2014) documented significant evidence of bio-based flocculant preforming well against standard synthetic flocculants (polyacrylicamide). Flocculation and centrifugation pairing is just one of many purification methods used in today's industries. THE IUPAC defines flocculation as, “a process of contact and adhesion whereby the particles of dispersion form larger-size clusters" (Slomkowski et al., 2011). To help sequester harmful environmental impacts associated with standard flocculant production, bio-based flocculant material has become a suggested alternative. Consequently, researchers have begun to explore renewable bio-based flocculants produced from animal co-products (Garcia et al., 2014). Extracted from chicken blood, erythrocyte hemoglobin has been shown to be a competitive alternative to standard flocculants such as poly(diallydimethylammonium chloride) (PDADMAC) (Piazza et al., 2014).

Although promising on paper, there is still a wide gap of information analyzing the economic and commercial viability of these by-product production cycles. One methodology of economic impact evaluation is a Techno-economic analysis (TEA). TEA modeling is an economic forecast tool which analyzes and compiles the fixed capital and variable costs and projects the annual rate of economic return and is usually associated with a commercial production process. A TEA appears to be an appropriate methodology to analyze the economic viability of full scale chicken by-product conversion operations. This sort of analysis can play an important role in the translation of benchtop discoveries to commercial application. A precursor study (Piazza et al., 2010) to this research undertaking developed a baseline estimate of the economic feasibility of a chicken blood-to-flocculant conversion plant. The analytic results demonstrated that two pounds of chicken blood flocculant are required to replace one pound of polyacrylamide (PAM) flocculant. Further, a chicken blood floccullant value of $0.60 per pound was calculated. It was also speculated that chicken blood flocculant could potentially replace 17% of the synthetic flocculant utilized annually in North America. Thus, insinuating that there are potential economic incentives and area for a commercial conversion process to start-up.

Since these conclusions were based on base-line assumptions, the need for further investigation of the economic viability of the proposed process is determined.

The objective of this study is to develop a TEA to determine the economic viability of our hypothetical chicken blood-to-flocculant operation. Further, the research focused on determining which unit operations, materials, and overall accompanying costs acquire the greatest economic impact. This analysis is set as precursor for future research endeavors looking to expand or refine the base process proposed.

Materials and Methods

Based on analytical data, contemporary production processes, and quoted equipment and supply values from industry representatives, a model of a flocculant production facility was produced, which estimated the capital, variable, and overall overhead costs for commercial conversion of bio-based flocculant from chicken blood. This model is designed to gauge the overall economic rationality of chicken blood to flocculant production. This model is not meant to replace a final design and construction of a plant, but for proof of concept relative to this theoretical scheme.

Certain aspects of this analysis were dependent on the location of the proposed facility. Specifically, the transportation costs, utilities, and sewer surcharges were directly related to the proposed location. This analysis is based on a plant located in Savannah, Georgia, and the location is the basis of the sewage surcharge formula, utility rates, and distance traveled for raw material acquisition. Savannah, Georgia is a major chicken production region (Bishop Jr. et al., 2015), and the analysis makes the assumption that there are at least three poultry processing plants within a 20 mile driving distance. Using poultry processing statistics (250,000 average sized chicken processed daily and total collected blood per head) documented in a 2009 study (Kiepper et al., 2009), the chicken blood conversion plant was calculated to processes approximately 92,000 gallons of blood per day and produces roughly 39,200 kg of flocculant daily. Main unit operations include: transportation, screening, washing blood cells, lysing blood cells, cell solid removal, dehydration, and packaging. A schematic of the extraction of hemoglobin to produce bio-based flocculant is shown in Fig. 1.1.

Presently, information regarding design parameters and operating constraints is limited. Assumptions are presumed based off of lab scale analytical data and flow rates required to process the chicken blood amount received daily. To produce the daily amount proposed, a semi-continuous process needs a minimum flow rate constraint of 192 gpm. The overall equipment processing and input-output diagram is shown in Fig. 1.2. This diagram helps illustrate where waste streams are produced and helps clarify the overall product flow throughout each stage of operation. Parallel to Fig. 1.2., a itemization of product mixture components throughout main process operations is detailed in Table 1.2. This table depicts where and how specific materials are (EDTA, saline, etc.) as well as detailing the steps needed for hemoglobin protein isolation. The hypothetical scheme begins with chicken blood acquisition from nearby processing plants. Before being transported to the flocculant production facility the chicken blood is mixed with ethylenediaminetetraacetic acid (EDTA) which prevents coagulation. The blood is then transported by tanker truck to the flocculant facility. Chicken blood is pumped and screened through a Rotary Vacuum Filtration Device (RVFD), which removes unwanted solids contained within the blood (e.g. feather, feces, and egg shell fragments). Once screened, the blood is stored in a surge tank, if immediately processed. Blood cells are washed utilizing two centrifugation and decantation cycles, which removes blood serum and leaves blood cells suspended in saline.

The decanted serum is disposed in the plants waste water stream. To extract hemoglobin the cells are lysed using a system of industrial size ultrasonic processors. Once lysed, unwanted cell solids are centrifuged out and a hemoglobin water solution remains. To achieve powdered flocculant product, a spray dryer dehydrates the hemoglobin to less than 1% w/v moisture. Dry bio-based flocculant is packaged and sold to the consumers. The machine process illustration is shown in Fig. 1.2.

Transportation

Chicken blood is acquired from a nearby processing plant and transported to the flocculant facility using a 33,000 gal semi-tractor trailer rig. Each day, three round trips to processing plants are hypothesized. Each trip yields roughly 30,700 gallons of blood, the estimated daily bleed out volume for a processing plant. Estimation of vehicle tax, insurance, and variable costs associated, on a per mile basis, were modeled using national average values, based on truck weight class, detailed in the American Transport Research Institute’s (ATRI) Analysis of Operation Costs of Trucking: 2010 (Trego et al., 2010). Total fuel consumption (gal.) was modeled using eq. (1) and (2).

(1) $\text{Composite MPG} = 1/(1/(\text{MPG City}) \times \%\ \text{City} + 1/(\text{ MPG Highway}) \times \%\ \text{Highway}$

(2) $\text{Annual Fuel Consumption} = (\text{Yearly Miles Driven})/(\text{Composite MPG})$

Where: MPG City is the city fuel economy of a vehicle in miles per gallon (mpg), % City is the total percentage of driving done on city miles out of total miles driven (%), MPG Highway is the highway fuel economy of a vehicle in miles per gallon (mpg), % Highway is the total percentage of driving done on highway miles out of total miles driven (%). Annual fuel cost was estimated using the 2014 national diesel price per gal ($/gal). The fixed and variable costs associated with transportation were calculated on a per mile rate based on the U. S. national average, which are detailed in ATRI's 2010 catalog (ATRI, 2010) and shown in table 1.3. The fixed and variable costs include: vehicle taxes, vehicle insurance, license fees, fuel, oil, tire wear, maintenance, labor, and repair. The transportation is assumed to have a 10 year depreciation period, based on total useful life expectancy, as well as an assumed 9% interest rate on total capital. Additionally, the salvage value was assumed to be 15% of total transportation capital.

Mixing and Screening

When the blood arrives at the production facility it is pumped from a truck using a cutter pump, which will crush large solids left in the blood. The blood is then pumped through a RVFD, which extracts the large solids from the liquid. Once large solids have been removed the blood is pumped into a surge tank, where it is stored until processing. The cutter pump proposed was a Cornell 4NNTL Cutter Pump, and the RVFD was a Komline-Sanderson RVFD. Quoted equipment cost figures were obtained by consultation of company representatives. Equipment selection was based on these key constraints: specific gravity, flow rate, density, and viscosity.

Washing Cells

The blood is moved from the surge tank to the decanter centrifuge using a slurry pump. The decanter centrifuge removes the serum through decantation. After, the blood serum is replaced with and equal amount of PBS. To keep the process continuous, and efficient, the Blood-PBS mixture is pumped to a second centrifuge. The liquid is centrifuged and decanted out and the blood is suspended in a half volume of PBS relative to the original serum amount. The decanted serum and PBS is placed into the wastewater stream for removal. The slurry pump proposed was a Cornell 2SPR Slurry Pump, and the two decanter centrifuges suggested are

Hiller DecaPress Two-Phase Decanter Centrifuges (DP45-422). The quoted capital costs associated with these machines were obtained consultation with equipment manufacturer representatives.

Lysing Cells and Cell Solid Removal

After washing, the blood cells and PBS remain. The mixture is pumped into a holding tank before ultrasonic processing. A doughnut horn attachment, attached to the holding tank, is proposed for upholding the continuous operation. From the holding tank, blood is pumped into a matrix of six ultrasonic processors. Six ultrasonic processors were selected in order to meet the operation's flow rate requirements. The ultrasonic processors lyse the red blood cells and uncase the hemoglobin protein. The lysed cell material and PBS mixture is pumped to a third centrifuge, where suspended cell solids are removed. The remaining mixture is comprised of hemoglobin protein and PBS solute. The ultrasonic processor chosen was a Hielscher Ultrasonics UIP1000 processor. The proposed centrifuge was the same model stated in the washing cells section. Again, quoted capital costs were obtained through consultation with manufacturer representatives.

Dehydration

The left over PBS-hemoglobin slurry mixture is pumped to series of three spray dryers. The spray dryers dehydrate the hemoglobin to a moisture content of less than 1%. The left over material is a bio-based powder flocculant. The spray dryer utilized is a LPG800-10000 high-speed centrifugal spray dryer. This particular spray dry was selected based off its variable flow rate and wide array of application (ceramic, dairy, polymer, fertilizer, and organic compound products).

Waste Stream Surcharge

Due to the high water pollutant characteristics of blood, and high costs associated, sewage surcharge was an area of particular focus for this project. Online research of the Savannah, Georgia surcharge calculation methodology found that eq. (3) was utilized by a majority of waste water treatment processors.

(3) $\text{Surcharge} = V \times (B - C) \times 8.34 \times \text{Cost Factor}$

Where: V is the gallons of water per million gallons, B is the total contribution from user in mg/L, C is the normal domestic sewage strength (allowable), 8.34 is the conversion of pounds per gallon, and Cost Factor is the cost factor for the surcharge characteristic considered in $/lb.

Economics

The economic model was developed using Microsoft Excel 2013 spreadsheet software. The software was used to compile the capital and variable costs throughout the process. An in-depth analysis of all capital and variable costs considered is documented in Table 1.6. Capital costs included all equipment, trucks, and the initial cost of the building and land. Additionally, the variable costs included: wages, utilities, materials, administration, maintenance, repair, insurance, and depreciation costs, which accumulate during equipment and property use. A 10 year depreciation period was assumed. A straight-line-depreciation method was used to calculate the consumption pattern of the capital over its intended useful life, and to generate salvage value estimates. To estimate the selling price of flocculant produced, a break-even chart was developed and is shown in Fig. 1.5. To generate an estimate of annual revenue eq. (4) was used.

(4) Annualized Capital Cost =Total Annual Benefit-Total Annual Fixed Cost-Total Annual Variable Cost

Where: total annual benefit accounts for the income produced from product sale and equipment salvage, total annual fixed cost is the summation of annualized capital cost and depreciation, insurance, and taxes relative to the fixed capital, and total annual variable cost is the summation of all annual variable expenses. To annualize capital cost the total capital investment was multiplied by an annualization factor calculated using eq. (5).

(5) $A(r,n) = (r(1+r))^n/((1+r)^n-1)$

Where: r is the prevailing rate of interest (assumed to be 0.05), and n is the usable life time of the capital asset (assumed to be 10 years). To analyze the capital and variable costs that have the greatest economic impact, Microsoft Excel pie charts were developed. Further, sensitivity analyses, including theoretical economy scales (annual cost vs. production rate) and cash modeling (annualized cash flow vs. production rate), were produced to determine the most efficient flocculant price point.

Results and Discussion

Relative to the transportation scenario described above, a summarization of all transportation capital and variable costs are shown in Table 1.3. The cost of the trucks made up a majority of the transportation capital at 105,000 USD. The fuel and labor costs maintained the largest portion of annual transportation variable costs at 7,263 and 6,505 USD respectively. The vehicle insurance and vehicle taxes are relatively low. Since the model calculates these costs on a per mile basis, and only one truck is assumed to travel 60 miles per day, these costs are not reflective of a real world process simulation, but are focused as attestation of the operation's feasibility.

Due to diluted serum components retaining high wastewater pollutant characteristics, the economic impact of annual waste water surcharge was speculated to become a main, if not the, deciding factor of the feasibility of this process. Accordingly, calculation of annual sewage surcharge was based on rigorous analytical testing of chicken blood pollution characteristics (BOD, TSS, COD, and NH3). The calculated sewage surcharge cost may be viewed on Table 1.4. Naturally, chicken blood sustains high COD at 106,350 mg/L, thus, incurred roughly 70% of the annual surcharge cost at 197,421 USD of 285,550 USD overall. A majority of the remaining associated cost was due to BOD at 86,619 USD annually. Surprisingly, TSS and NH3 rate charges were the most expensive at 0.22 and 0.45 USD per pound, but their surcharge cost impact was extremely low due to chicken blood's low inclusion of TSS and NH3 at 223 and 300 mg/L respectively. The TSS had no impact on cost because the volume was lower than the maximum surcharge-free amount, 250 mg/L.

The overall equipment capital cost was compiled in Table 1.5. The spray dryers make up over half of the overall initial equipment cost, 1,350,000 USD of 2,376,304 USD. To process the liquid material at the processes constrained flow rate, 192 gpm, three separate spay dryers are considered. Further, the decanter centrifuge and RVFD incurred a relatively high price quote of 150,000 USD each, therefore, producing a large initial capital investment. Due to the relatively low flow rate of the ultrasonic processors, approximately 35 gpm, six separate processing reactor units are considered for this operation, and incurred an overall cost of 270,000 USD. Variable costs associated (equipment maintenance (assumed 3% of capital), depreciation

(10 years), insurance (5%), and repair (2%)), which are not shown, produced a total annual cost of approximately 473,000 USD.

The pie chart analysis (Fig. 1.3-1.4) of total variable and capital costs produced results previously hypothesized. Sewage surcharge was shown to make up 49% of the total overall variable cost, which demonstrates the incentive for processing plants to dispose their excess chicken blood through other means than waste water streams. Surprisingly, the materials made up 21% of total variable costs. This is due to the relatively high volume of EDTA purchased, which is used to anti-coagulate the raw income of chicken blood. A majority of the capital cost was made up of initial construction costs, at 39%, and the initial investment on spray dryers, at 33% respectively. The overall cost analysis is detailed in Table 1.6. After annualizing the overall capital cost and summation of yearly fixed costs (depreciation, insurance, taxes) the annualized fixed cost of approximately 872,000 USD was calculated. Total annual variable costs incurred an overall cost of approximately 7,000,000 USD. To overcome the overhead of these two costs, the total annual benefit, consisting of economic benefit from salvaged equipment and packaged flocculant sold, had to equal the sum of the annualized variable and fixed costs. At 85% process efficiency assumed, the total flocculant capacity of approximately 10,000,000 kg/yr was calculated. Assumed to sell at a rate of 1 USD per kg, the total annual benefit produced roughly 10,000,000 dollars, including equipment salvage. Thus, the overall projected annual revenue resulted in roughly 2.4 million dollars. This value was calculated assuming that 100% of produced flocculant would be sold to consumers. The break-even point analysis (Fig. 1.5), which assessed the break-even unit (BEU) at a unit (flocculant) price of 1 USD per kg, resulted in a BEU of approximately 2,760,000. Consequently, to break even nearly 28% of product produced would need to be sold before profit is obtained. From the current prospective, and all things considered, the process is projected to be highly economically feasible.

Implications

The relatively high profit margin projected resulted from acquiring the initial raw chicken blood at no cost, which is a consequence of chicken processers not wanting to dispose of the chicken blood, since it is an expensive procedure. Comparatively, a 2013 study (Anthony, 2013) documented the production of an algae derived flocculant, which incurs large raw material production costs since the algae culture must be grown and cultivated. The ethanol production industry must pay for raw substrate sources, which decreases the profit area substantially (Pimental and Patzeck, 2005; Kwiatkowski et al., 2006; Kazi et al., 2010). If the operation theorized becomes exceedingly profitable, the chicken processing plants will undoubtedly start to sell chicken blood for their own profit. This phenomenon has been documented in similar applications; a feasibility analysis focused on scrap tire to crumb rubber conversion (Sunthonpagasit et al., 2003) detailed the high demand for rubber raw materials (tires) causing increase in tipping fees and transportation costs within the acquisition territory. Future market consequences, such as described, may change the high profit rate currently predicted. Further, the selling performance of packaged flocculant depends on a variety of factors: performance versus current commercial flocculant, product application, consumer, etc. Looking back at the precursor study (Piazza et al., 2011), areas of greatest economic impact presided in: facility overhead, labor, utilities, and sulfuric acid. Comparatively, the current study has concluded that initial equipment and building capital make up a majority of the costs, while labor making up a lower percentage of variable cost. The initial studied hypothesized that wastewater surcharge may contribute to a large portion of the overall costs. It was found that this is indeed true for this study; the wastewater surcharge is roughly half of all variable costs. Next, the capital costs related to dehydrating the CKB posed relatively high facility charges. This study has shown this to be case as well; the utilities charge, especially from spray drying, was shown to be 20% of all overall variable costs. One of the biggest considerations is the performance of the bio-flocculant and how selling point is affected. It was projected that the cost of flocculant production will be $0.77 per pound (Piazza et al., 2011). After consideration of BOD removal, a total net cost of production is suggested at $0.33 per pound (Piazza et al., 2011). Compared to PAM, $1.20 per pound, CKB is effectively active at a 2:1 pound ratio, yielding a renewed CKB production cost of $0.66 per pound (Piazza et al., 2011). At half the cost of PAM, CKB may have a great economical/environmental effect in the poultry processing industry. This study assumed a base-line value of $0.45 per pound, which is lower than previously projected in the 2011 study. Therefore, since the assumed value is lower than previously projected, this study suggests that there may be even better economic feasibility if the selling point is increased to $0.66 per pound. Therefore, future research, using this study as a precursor, may benefit from in-depth analysis of selling point interactions, such as market response, transportation, and selling ability.

Conclusion

The techno-economic analysis evaluating the hypothetical chicken blood-to-flocculant operation suggests an economically feasible process with a high profit projection. The high profit projection is a result of free raw chicken blood acquisition and a surplus of product, which results large room for potential profit. The analysis has shown sewage surcharge has a dramatic effect on overall cost, therefore, future research may benefit from focusing on applications which lowers the pollutant characteristics of chicken blood. While there is undoubted economic feasibility for new-entrant chicken blood conversion plants, there are also considerable market uncertainties, described above, which permit cautious analysis. While carrying out this analysis many new questions arose. Does centrifugation of cell solids and serum affect the overall performance of the flocculant produced? Is it economically beneficial to centrifuge the serum and cell solids out of the solution? This underlying analysis provides an effective precursor for new research endeavors focusing on answering these uncertainties.

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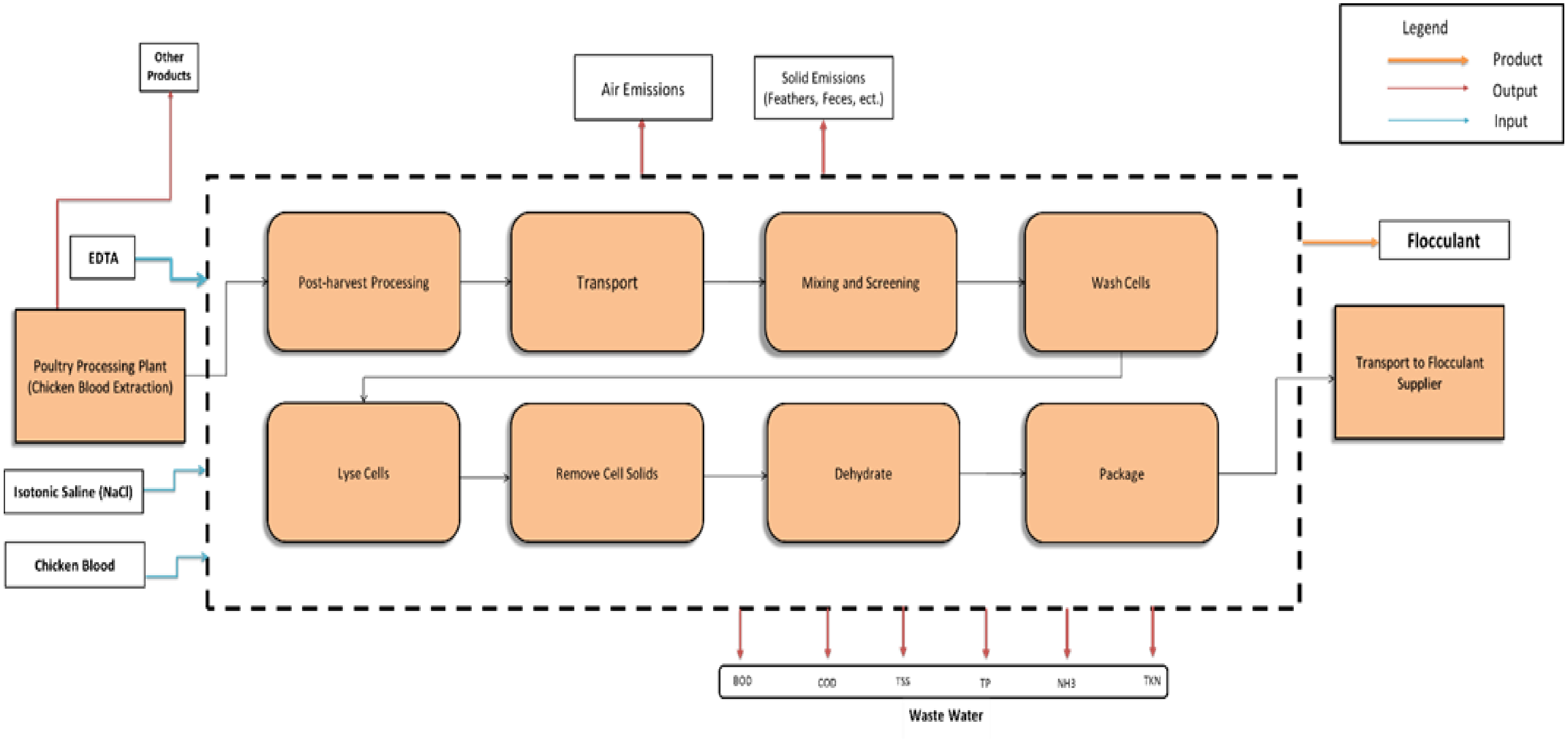

Figure 1.1. Basic process flow diagram

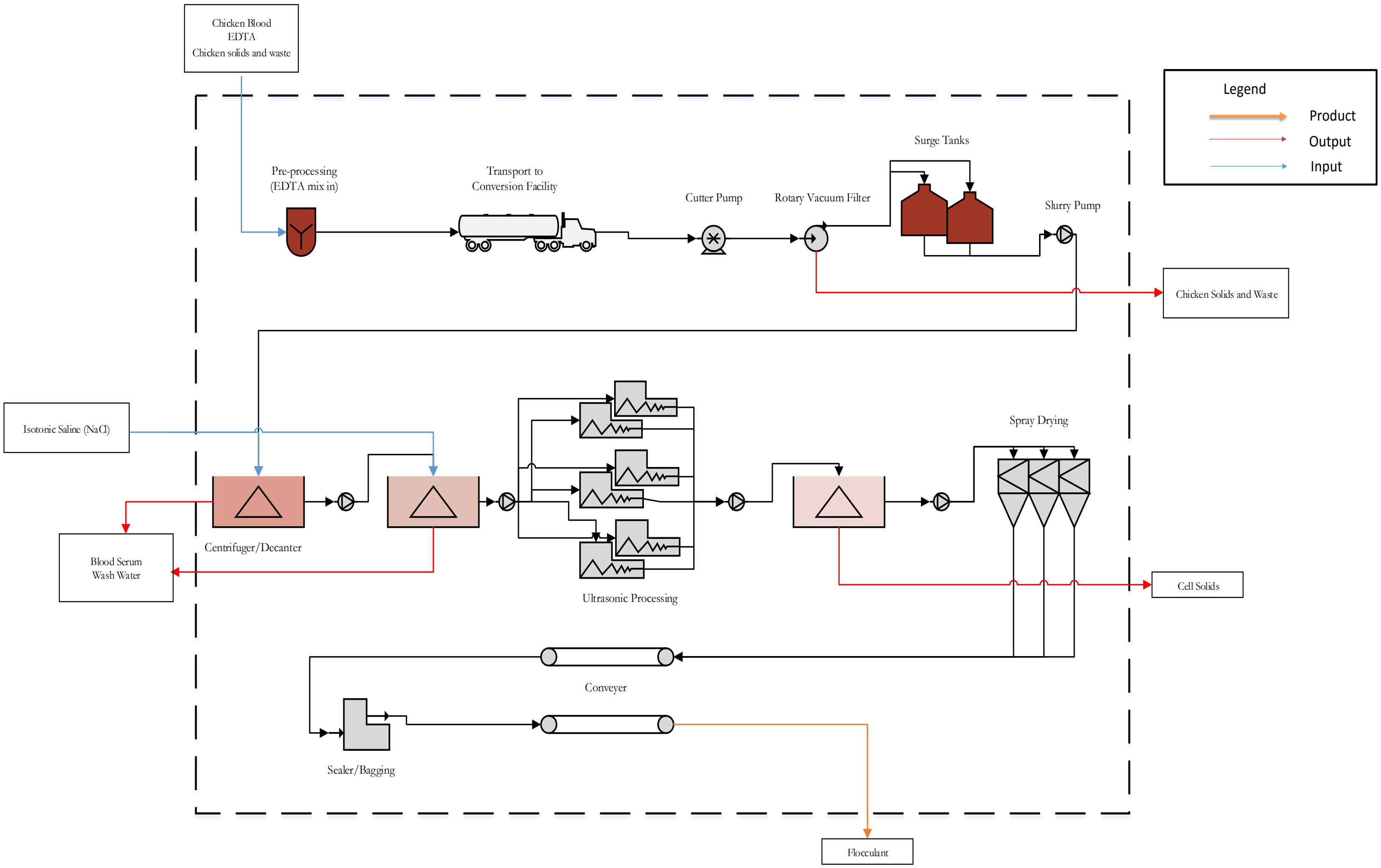

Figure 1.2. Equipment based input-output process diagram

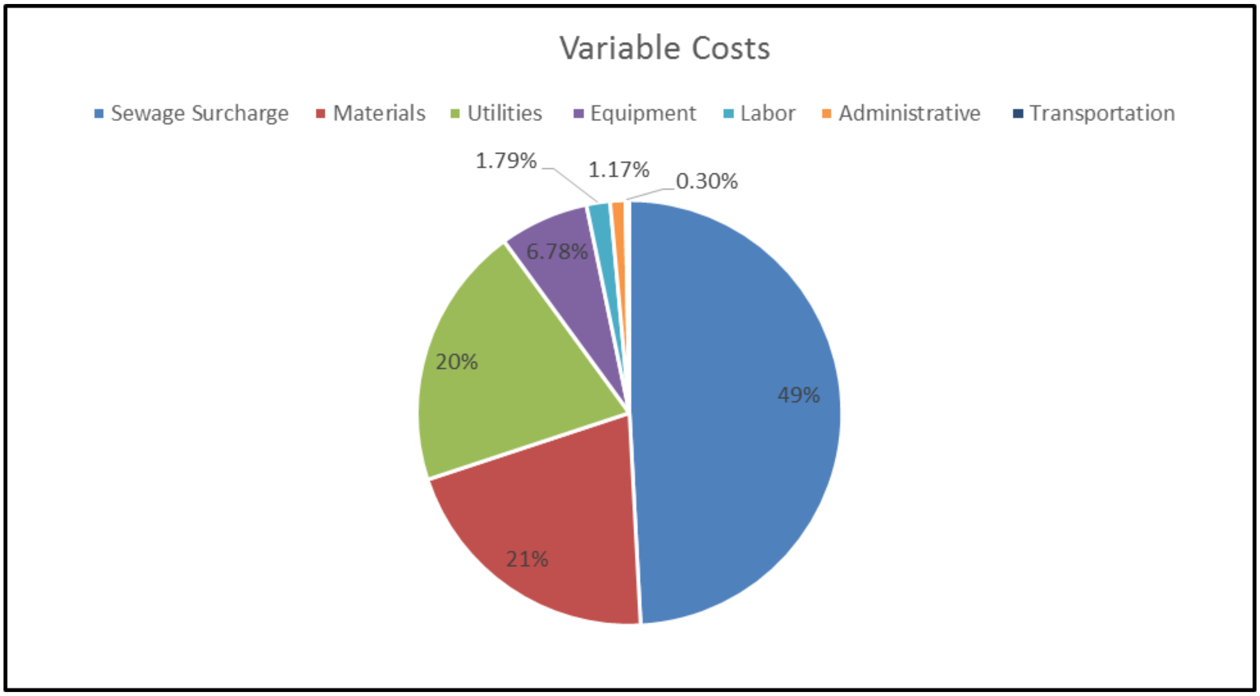

Figure 1.3. Economic impact distribution of variable costs

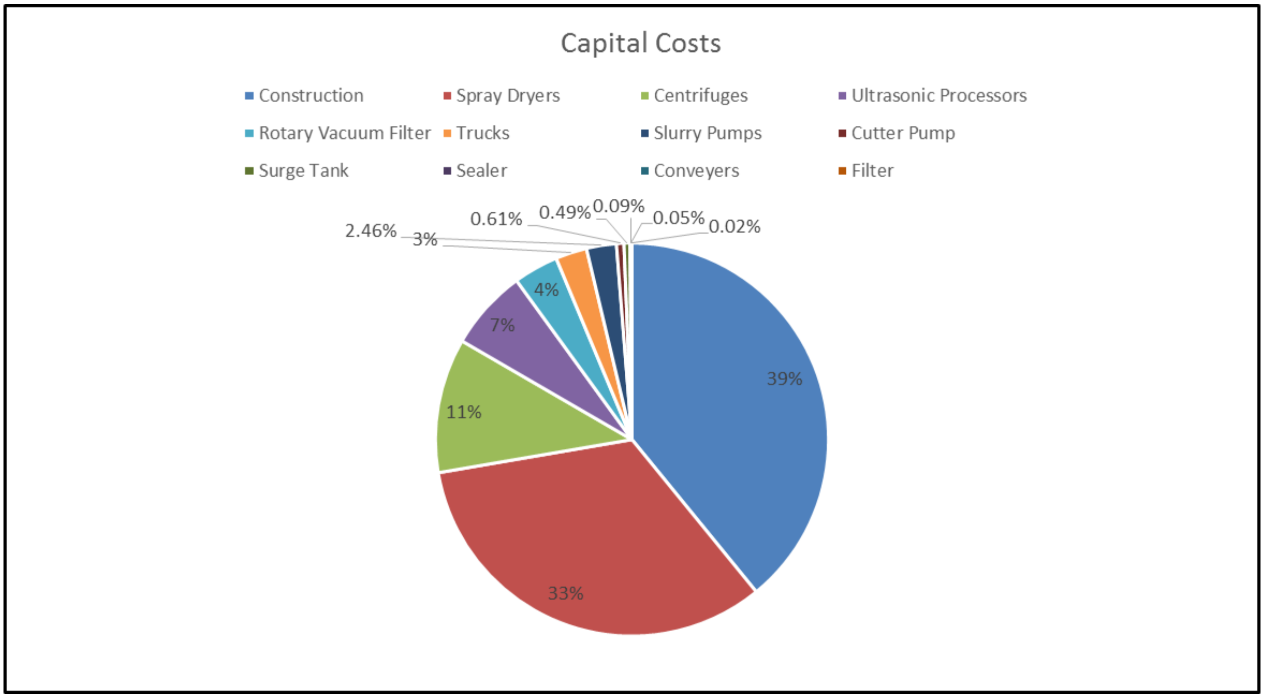

Figure 1.4. Economic impact distribution of capital cost

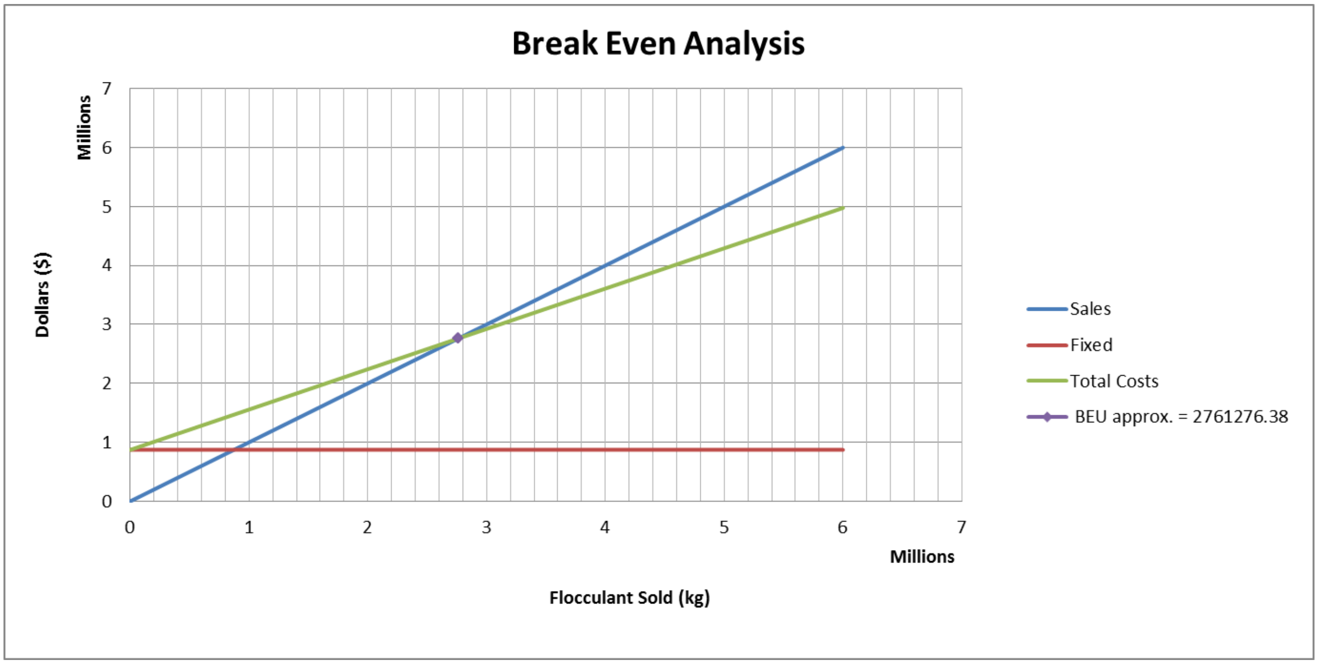

Figure 1.5. Break-even point analysis

Table 1.1. Overall assumptions list

Overall Assumptions			
Initial Factors	**Amount**	**Unit**	***Source***
# of chickens daily	750000.00	heads	*(Kiepper, 2009)*
Average weight of chicken	5.92	lbs	*(Kiepper, 2009)*
Blood percentage of total mass	0.08	Percent	*(Kiepper, 2009)*
Amount Blood/Bird	0.44	lbs	*(Kiepper, 2009)*
No. of Birds Processed Daily	750000.00	heads	*(Kiepper, 2009)*
Total Weight of Blood daily	333000.00	lbs	*(Kiepper, 2009)*
Total Bleed-Out Weight	166500.00	lbs	*(Kiepper, 2009)*
Total Bleed-Out Volume	23735106.54	gal/year	*Calculated*
Gallons per day	91288.87	gal/day	*Calculated*
Gallons per hour	11411.11	gal/hr	*Calculated*
Work days in year	260.00	days	*Assumed*
Hours per day	8.00	hours	*Assumed*
Blood Trandsportation Distance (round trip)	20.00	miles	*Assumed*
Trips per day	3.00	trips/day	*Assumed*
Labor	4.00	workers	*Assumed*
Wage	15.00	$/hr	*Assumed*
Process efficiency	85.00	%	*Assumed*
Raw Materials	**Amount**	**Unit**	***Source***
Blood	95238000.00	kg/yr	*Calculated*
Water	125904064.57	gal/yr	*Analytical Data*
EDTA	134770.66	kg/yr	*Analytical Data*
Isotonic Saline	127047492.00	kg/yr	*Analytical Data*
Serum	63523746.00	gal/yr	*Analytical Data*
Hct	38095200.00	gal/yr	*Analytical Data*
Cell Debris	5295232.80	kg/yr	*Analytical Data*
Other Cell Pts	23815256.23	kg/yr	*Analytical Data*
Hb	8984710.97	kg/yr	*Analytical Data*
NaCl	1143427.43	kg/yr	*Analytical Data*
(Blood+EDTA)	95372770.66	gal/yr	*Calculated*
(Hct+1/2PBS)	101618946.00	kg/yr	*Calculated*
(Hb+Water)	71936743.25	gal/yr	*Calculated*
Water (kg/hr)	30265.40	kg/hr	*Calculated*
Total Solid Cell Debris (metric ton)	29110.49	ton	*Calculated*
Utilities	**Amount**	**Unit**	***Source***
Gas Rate	$12/million btuh	$	*Savannah, GA Utility Rate, 2015*
Electricity Rate	0.14501 cents/kWh	cents	*Georgia Public Service Commission, 2015*
Water Rate	$13.2 + $1.62*(cu ft used)	$	*Savannah, GA Utility Rate, 2015*
Tippage Rate	$34.92/ton	$	*(van Haaren, 2010)*
Transportation	**Amount**	**Unit**	***Source***
Insurace	0.06	$/mile	*American Transport Research Institute, 2015*
Vehical Tax	0.03	$/mile	*American Transport Research Institute, 2015*
License Tax	0.02	$/mile	*American Transport Research Institute, 2015*
Oil	0.02	$/mile	*American Transport Research Institute, 2015*
Tire wear	0.04	$/mile	*American Transport Research Institute, 2015*
Maintenance	0.14	$/mile	*American Transport Research Institute, 2015*
Labor	0.42	$/mile	*American Transport Research Institute, 2015*
Repair	0.15	$/mile	*American Transport Research Institute, 2015*
Salvage Value	0.15	$/mile	*American Transport Research Institute, 2015*
Sewage Surcharge	**Amount**	**Unit**	***Source***
Blood BOD Content	46725.00	mg/l	*Analytical results*
Blood COD Content	223.00	mg/l	*Analytical results*
Blood TSS Content	106350.00	mg/l	*Analytical results*
Blood NH3 Content	300.00	mg/l	*(Hansen and West, 1992)*
BOD Allowable	250.00	mg/l	*Savannah, GA surcharge rates, 2015*
TSS Allowable	225.00	mg/l	*Savannah, GA surcharge rates, 2015*
COD Allowable	425.00	mg/l	*Savannah, GA surcharge rates, 2015*
NH3 Allowable	12.00	mg/l	*Savannah, GA surcharge rates, 2015*
Materials	**Amount**	**Unit**	***Source***
Isotonic Saline	0.75	$/kg	*molbase*
Plastic Bags (50 lbs)	0.39	$/bag	*U-Line 50 lb bag*
EDTA	3.00	$/kg	*molbase*
Construction	**Amount**	**Unit**	***Source***
Equipment freignt	6.79	% of Capital	*NYU Capital Cost by Sector*
Installation	10.00	% of Capital	*NYU Capital Cost by Sector*
Piping	7.00	% of Capital	*NYU Capital Cost by Sector*
Instrumentation and Control	8.51	% of Capital	*NYU Capital Cost by Sector*
Electrical	10.00	% of Capital	*NYU Capital Cost by Sector*
Buildings	11.50	$/sq. ft	*Global,1994*
Yard Improvement	2.30	% of Capital	*NYU Capital Cost by Sector*
Land	109154.93	$/acre	*ASABE, 2008*
Engineering	8.19	% of Capital	*NYU Capital Cost by Sector*
Contingeacy	6.43	% of Capital	*NYU Capital Cost by Sector*

Table 1.2. Mass balance of liquid throughout the process

% of mixture after process			**Cell Solid Debris**				
Process	**Water**	**Serum**	Cell Membrane	Cell Organelles	**Hb**	**EDTA**	**NaCl**
0. Raw Income	-	66.61%	5.55%	24.97%	9.42%	0.14%	-
1. Wash Cells	61.95%	-	5.21%	23.44%	8.84%	-	0.56%
2. Lyse Cells	61.95%	-	5.21%	23.44%	8.84%	-	0.56%
3. Remove Solids	87.51%	-	-	-	12.49%	-	-
4. Dehydration	-	-	-	-	100.00%	-	-

Table 1.3. Economic distribution of transportation costs

Capital Costs	($)
Trucks	$105,000.00
Total Capital Cost =	$105,000.00
Fixed Costs	($/yr)
Insurance	$982.80
Vehicle Taxes	$429.00
License fees	$343.20
Total Fixed Cost =	$1,755.00
Variable Costs	($/yr)
Fuel	$7,263.01
Oil	$312.00
Tire wear	$686.40
Maintenance	$2,152.80
Labor	$6,505.20
Repair	$2,308.80
Total Variable Cost =	$19,228.21
Other Cost Considerations	($/yr)
Depreciation (over 10 years)	$8,925.00
Interest (9% based on GMC website)	$9,450.00
Total Other Cost =	$18,375.00
Equipment Salvage Value	
Salvage Value (Assuming 15%)	$15,750.00

Table 1.4. Sewage surcharge cost analysis

Whole Charge Variables	Amount (mg/L)	Rates ($/lb)	Surcharge (Monthly Basis) ($)	Surcharge (Daily Basis) ($)
SERUM :				
BOD =	46,725	$0.16	$86,619.31	$2,887.31
TSS =	223	$0.22	$0.00	$0.00
COD =	106,350	$0.16	$197,421.19	$6,580.71
NH3 =	300	$0.45	$1,509.66	$50.32
		Total:	$285,550.16	$9,518.34

Table 1.5. Process equipment list

Equipment	Model	Units Needed	Single Unit Cost ($)	Total Initial Cost ($)
Surge Tank	3500 Gallon DW Tank	2	$9,876.95	$19,753.90
Spray Dryer	LPG800-10000 High-speed centrifugal Spray Dryer	3	$450,000.00	$1,350,000.00
Ultrasonic Processor	Model UIP10000 - Ultrasonic Processor with "donut" horn	6	$45,000.00	$270,000.00
Centrifuge	Hiller DecaPress Two-Phase Decanter Centrifuge (DP45-422)	3	$150,000.00	$450,000.00
Cutter Pump	Cornell 4NNTL Cutter Pump	1	$25,000.00	$25,000.00
Slurry Pump	Cornell 2SPR Slurry Pump	5	$20,000	$100,000
Sealer	HS-BII Rotary Sealer	1	$3,550.00	$3,550.00
Bagger	Stand Pouch Packing machine	1	$5,000.00	$5,000.00
Conveyor	SB/HD electric conveyor 20 ft	2	$1,000.00	$2,000.00
Filter	KuoBao Same Design chemical liquid filter	1	$1,000.00	$1,000.00
Rotary Vacuum Filter	Komline-Sanderson RDVF	1	$150,000.00	$150,000.00
			Total =	$2,376,303.90

Table 1.6. Overall cost analysis

		Scheme 1	
Equipment lifetime	[year]		10
Blood capacity	[gal/hr]		11411.11
capacity for flocculant (85% Yield Efficiency)	[kg/hr]		4898.71
Total Flocculant Capacity	[kg/yr]		10189313.42
Total initial cost	[$]	$	2,476,303.90
Equipment freignt	[$]	$	168,141.03
Installation	[$]	$	247,630.39
Piping	[$]	$	173,341.27
Instrumentation and Control	[$]	$	210,733.46
Electrical	[$]	$	247,630.39
Buildings	[$]	$	69,000.00
Yard Improvement	[$]	$	56,954.99
Land	[$]	$	54,577.47
Engineering	[$]	$	202,809.29
Contingeacy	[$]	$	159,226.34
Total fixed capital cost	[$]	**$**	**4,066,348.53**
Annualized capital cost	[$/yr]	$	526,610.74
Equipment salvage value	[$/yr]	$	39,513.04
Benefits(Packaged Floc)	[$/yr]	$	10,189,313.42
Benefits(Trans. Blood)	[$/yr]	$	-
Total annual Benefit	[$/yr]	**$**	**10,189,313.42**
Depreciation	[$/yr]		$48,709.77
Insurance	[$/yr]	$	123,815.20
Taxes	[$/yr]	$	173,341.27
Total Annualized Fixed Costs	[$/yr]	**$**	**872,476.98**
Total annual variable costs	[$/yr]	**$**	**6,969,809.05**
Projected Annual Revenue	[$/yr]	**$**	**2,347,027.38**

CHAPTER IV:

CRADLE-TO-GRAVE LIFE CYCLE IMPACT ASSESSMENT AND TECHNO-ECONOMIC ANALYSIS FOR POLY(LACTIC ACID) (BIO) COMPOSITES

Abstract

This research endeavor focused on a life cycle impact assessment (LCAI) and techno-economic analysis (TEA) comparison LCA of poly(lactic acid) (PLA) composite production, using both organic and inorganic fillers. Organic fillers DDGS, flax, hemp, rice husks, and wood are compared against inorganic substitutes (glass and talc) for PLA plastics. This study utilized LCAI and TEA methodology to estimate and quantify costs, emissions, and energy intensity (EI) associated with material acquisition, processing, transport, and end of life treatment used during plastic composite production. Emission categories analyzed include Global Warming Potential (GWP), Air Acidification (AA), Air Eutrophication (AE), Water Eutrophication (WE), Ozone Layer Depletion (OLD), Air Smog (AS), High Carcinogens (HC), and High Non-Carcinogens (HNC). To achieve a “Cradle-to-Grave” perspective, two models were meshed, the Plastic Comparator (PC) and EIO-LCA (EIO), to simulate the EI and emissions associated over the entire life cycle. Based assumptions used, this research has shown that utilizing land fill end of life treatment and glass filler composite was the most environmentally harmful option, and maintained the highest economic impact, for all impact categories during PLA composite production. Alternatively, both DDGS and wood filler composites paired with recycling end of life treatment were shown to be the least environmentally damaging method and incurred the lowest cost of all PLA composites considered. This study also suggests that utilization of organic bio fillers produces a lower economic/environmental impact, and EI, compared to utilization of

inorganic fillers in PLA composites. Accordingly, this research has demonstrated the impact of LCA/TEA paired analysis when assessing the bioplastic and biocomposite processing, which may be utilized as a precursor for parallel research undertakings.

Introduction

Plastic production has become one of the leading industries in our modern society and has consistently been transformed to fit the needs of our growing population. Plastic materials maintain many assorted properties that out-compete materials composed of wood and metal, and, in turn, plastics have procured a hefty world demand (Rosato, 2003). Since the 1950s, there has been an increasing trend in demand for plastics and is anticipated to increase steadily within the next 50 years (Plastics Europe, 2008). As our world population exponentially lurks closer to our projected sustainable limit (Smith, 1999), increasing plastic sustainability has become a leading issue globally (Morris, 2001). To counter act the current petroleum-based dependence, the substitution of bio-based plastics as a replacement, and or drop-in resource, for petroleum-based plastics has been shown to be a favorable solution. Bio-based materials entail a diverse range of renewable resources that can be fully recycled, or composted, and has potential to create sustainable, energy proficient, plastic processing.

Bio-based plastics come from a family of materials that can be extensively different from one another and are moderately or entirely based from natural resources (Erwin, 2003). Bio-based plastics include, but are not limited to: bio-polyethylene (BPE), poly(lactic acid) or polylactide (PLA), polyamide 11 (PA 11), PHA derived poly-3-hydroxybutyrate (PHB), and thermoplastic starch (Erwin, 2003). Biodegradable plastics, considered non-bioplastics, include fossil based polybutylene terephthalate (PBT) and polycaprolactone (PCL) (Erwin, 2003).

Bioplastics are obtained from a variety of different sources. The bioplastic industry generally uses starch, cellulose, glucose, and biomass oils to develop the current generation of bio-based plastic. Since early production of bio-based plastic in 1926, natural fibers such as lignin and cellulose have been used as natural reinforcement materials used in composites (John, 2008). Bio-based composite material has been shown to decrease the amount of petro-based plastic produced, thus, lowering the environmental burden released during production. One research study (Alvarez-Chaves, 2012) has shown that starch, PLA, and PHA bio-based composites have potential to lower fossil fuel use and sequester harmful health and environmental impacts. One current drawback associated with some bio-based plastics is due to extra processing of biological materials. Since many organic fibers utilized are plant based, the moisture content must first be lowered through various drying techniques (Gander, 1995). To attempt to quantify environmental impacts linked to bio-composite production, many plastic fabrication companies utilize SimaPro modeling software to project the overall environmental impact of plastic production potentially covering an entire cradle-to-grave commercial operation (Madival, 2009; Erwin, 2003). Currently, there are very few publications which compare LCA results over different combinations of filler, end of life treatments, and production parameters. Recent publications are solely focused on a single plastic or product and are usually limited to plastic processing research divisions (Madival, 2009; Erwin, 2003). Many plastic processors may benefit from a comparison tool which draws SimaPro database results and compares environmental impacts on a per kg basis. While similar models have been produced (Erwin, 2003), results are normalized to a single plastic production scheme, which makes comparison between alternative fillers and plastics difficult.

A LCAI approach involves the cradle-to-grave consideration for all operations in a functional unit's development. Product development steps include: extraction of raw materials, the acquisition of energy for the procedures and the transportation between them; processing and fabrication of preliminary materials; manufacturing of final product and distribution, and end-of-life treatments. The main purpose of an LCAI is to determine the overall energy, material, waste, and emission impact of a product's full life cycle, as well as an analysis to determine indirect environmental effects (Owens, 1997; Klopffer, 1997; Curran, 1994). One methodology of economic impact evaluation is a Techno-economic analysis (TEA). TEA modeling is a market forecast tool which analyzes and compiles the fixed capital and variable costs and projects the annual rate of economic return and is usually associated with a commercial production process. For example, the United States government has utilized TEAs to assess the economic viability of biofuel production from a variety of raw materials (Kazi, 2010; US Dep. of Energy, 2009). A TEA appears to be a viable methodology to analyze the economic impact variations of composites filled with varying materials. If evaluated, this research study may reveal previously unknown filler and end-of-life combinations during PLA (bio)composite production.

The objective of this study is to develop a LCA comparison to estimate the energy intensities environmental impacts during production of PLA (bio)composites, using different fillers, processing and material constraints, and end of life options. Further, a secondary objective is to quantify environmental and economic impact differences between plastics filled with bio-based and inorganic synthetic filler material.

Materials and Methods

The two models utilized for this project: (1) the Plastic Comparator (PC) model in which overall processing costs, energy intensities, and greenhouse gas emissions between petrochemical and bio-based plastics are calculated and compared utilizing the M Base database, and (2) EIO-LCA (EIO), an economic input-output life-cycle assessment method which estimates material, energy, and emissions resulting from economic activity. Using a combination of these models, arrangements between PLA and PP (bio) composites were compared over various fillers and end of life options. The fillers included: glass, talc, DDGS, flax, hemp, rice husks, and wood pulp filler. Five different end of life treatments were compared for each combination of plastic and filler, these comprise: recycling, incineration, landfill, landfill + methane extraction, and a base no end of life option. Utilizing the PC model, energy intensity and emission production was combined over five system boundary operations which include: Raw Material Acquisition, Transportation, Manufacturing and Processing, Consumption, and End of life treatment. The model calculates processing costs on a “per part” ($/part) and “per kg” ($/kg) basis, using user entered, and data base, assumptions. “Per kg” ($/kg) basis is calculated using eq. (1)

$$(1) \quad K_{unit} = (K_{equip} + K_{el} + K_{maint})/M$$

Where: Kunit is the cost of pellet material on a “per kg” ($/kg) basis, Kequip is the cost of processing equipment including mixer, pelletizer, and extruder, Kel is the cost of electricity, Kmaint is the cost of maintenance, and M is the material amount processed. The overall part cost “per part’’ ($/part) is calculated using eq. (2)

(2) $K_{part} = K_{proc} + K_{mat} + K_{tool}$

Where: Kpart is the cost of a single part ($/part), Kproc is the processing cost of a single part including injection, molding, grinding, maintenance, and electricity, Ktool is the cost of injection molding, Kmat is the material cost. PC models were ran using one material size, 100,000 kg, and three different part sizes, 0.01, 0.1, and 1 kg. A detailed assumption list for the PC model can be viewed on table 2.1.

Since many of the raw material price data ($/kg) researched was varied, a cost range for each filler was produced. Three separate pricing sources were used for each filler, high, average, and low values were utilized to create a sensitivity analysis for filler processing costs incurred. A grouping of all production pricing data collected is shown on Table 2.2. The raw material data was inserted into the EIO model and the results were graphically organized (Fig. 2.2). Utilizing the EIO model, total overall production costs were collected relative to each end of life treatment, filler option, and part size. The total overall production costs were graphically modeled and compared by each separate part weight, this comparison is shown on Figure 2.13.

Utilizing the EIO model and researched filler pricing data, EPA TRACI impact categories and energy intensity was modeled on a “per dollar” basis. TRACI, or Tool for the Reduction and Assessment of Chemical and other environmental Impacts, is the standard environmental impact assessment developed by the Environmental Protection Agency developed specifically for United States industries. Using this standard, select impact categories were chosen for analysis. Impact categories include: Energy (J), Global Warming Potential (GWP), Air Acidification (AA), Air Eutrophication (AE), Water Eutrophication (WE), Ozone Layer

Depletion (OLD), Air Smog (AS), High Carcinogens (HC), and High Non-Carcinogens (HNC). Using the US Purchaser Price Model database developed for unlamented plastic profile shape manufacturing, each impact category was normalized to a “per dollar basis’’ (unit/$).

To normalize all comparison parameters, both models were mathematically combined to establish each impact category into a “per kg” basis (unit/kg). To achieve this eq. (3) was utilized as shown.

(3.1) $E_{cat} \times K_{unit} = X_{unit}$

(3.2) $\text{Unit}/\$ \times \$/\text{kg} = \text{Unit}/\text{kg}$

Where: Ecat is the normalized EIO impact category on a “per dollar” (unit/$) basis, Kunit is the cost of pellet material described above, Xunit is the EIO impact category normalized to “per kg” (unit/kg) basis. The overall process methodology may be viewed in Figure 2.11.

For each impact category, graphic comparison matrix plots were developed using Microsoft Excel. Each graph compares all seven fillers for a specific end of life treatment and part weight. End of life treatments are compared vertically, while part weight is compared horizontally. Each impact category matrix can be shown in figures 2.2-2.11. To determine overall mechanical properties of PLA composites, a mechanical properties table was compiled from published documentations, this may be viewed in Table 2.3. Using the combination of results produced from TEA, LCA, and mechanical properties analysis, application recommendations were suggested.

Results and Discussion

Before multiplying both model’s normalized values, the “per kg’’ ($/kg) PC model data was compiled and graphically compared for each part weight, filler, and end of life treatment (Fig. 2.2). The data suggested that glass filler composite production maintains the most expensive life cycle, while DDGS and wood filler are the lowest cost to produce per kg. This holds true over all end-of-life options. 0.1 kg and 1 kg part weight graphs showed the least amount of cost variance between filler options, and 0.01 kg showed a significant amount of cost variance between end-of-life options. Recycling was shown to have the greatest amount of cost impact by reducing the cost $1-$2 per kg for all fillers analyzed, while landfilling proved to be the most expensive option. When 1 kg part weight was implemented filler composite production was shown to be the most cost effective solution. Thus, suggesting a larger part weight will include a lower cost in pellet material production. The processing cost sensitivity analysis (Fig. 2.12) produced expected results for all fillers. It was observe a direct relationship between processing costs and initial raw material price; i. e. if raw input is increased then the total processing costs should increase as well, as it should. Since raw input price directly affects the model and does not indirectly affect other variables, these results suggested the model is correctly evaluating these interactions. The overall production cost models (Fig. 2.13) produced the most significant results economically. The model’s results show that recycling incurs and drastically lower overall end of life treatment options and for all filler materials. Alternatively, landfill treatment is shown to have the greatest economic impact over all parameters. The overall production costs, relative to fillers specifically, are shown to be significantly lower for rice husks, wood, and DDGS, as compared to glass and wood fillers. Therefore, the results suggested that it is more economically beneficial to produce PLA fillers with organic materials as compared to inorganics such as glass and talc.

After multiplying each model's normalized values using equation (3.1), the environmental impact categories could then be graphically compared. GWP generation (kgCO2eq/kg) was shown to follow a similar trend compared to cost (Fig. 2.3). Again, recycling end of life treatment paired with glass filler production produced the lowest amount of CO2eq generation over all part weights. DDGS, rice husks, and wood filler production produced the lowest amount of CO2eq when paired with recycling end of life option. Using 1 kg part weight was shown to produce the least, and lowest, amount of carbon emission for all filler and end of life treatments analyzed. Energy intensity (J/kg) comparison graphs followed a trend similar to other impact categories (Fig. 2.4). Most energy efficient method was shown to use 1 kg part weight, recycling end of life treatment , and utilize DDGS, rice husks, and wood filler composite production. The most energy intensive method utilized, 0.01 kg part weight, incineration end of life treatment, and glass filler composite production. Air acidification (kg Ne/kg) comparison graphs followed a trend similar to other impact categories (Fig. 2.5). The most emission efficient method was shown to use 1 kg part weight, recycling end of life treatment , and utilize DDGS, rice husks, and wood filler composite production. The most environmentally harmful method, from an air acidification view utilized, 0.01 kg part weight, incineration end of life treatment, and glass filler composite production. Almost exact trends may be observed in: Air Eutrophication (Fig. 2.6), Water Eutrophication (Fig. 2.7), Ozone Layer Depletion (Fig. 2.8), Air Smog (Fig. 2.9), High Carcinogens (Fig. 2.10), and High Non-Carcinogens (Fig. 2.11). The most emission efficient method was shown as follows: 1 kg part weights, recycling end of life treatment, and utilize DDGS, rice husks, and wood filler composite production. The most environmentally harmful method, from an air acidification view utilized, 0.01 kg part weight, incineration end of life treatment, and glass filler composite production. This is especially significant since these trends suggest that not only is it more environmentally beneficially to produce PLA filler with organic matter, but it is also more economically beneficial.

Mechanical Properties

Many polymer and composite applications utilize fillers to account for many unique and robust applications. This may include: thermal, chemical, electrical resistances, as well as increasing, or decreasing, strength, stiffness, and elasticity. This table 2.3 is a developed overview of mechanical strength characteristics for poly(lactic acid) composites. Data was compiled from previous studies examining different composite properties. Almost universally, data samples were performed three times to achieve standard deviation (n=3) ranges. Tensile strength, or the maximum stress withstood before failure, was shown to be diverse for each filler and filler composite percentage. Examining PLA values suggests a high TS (MPa) linked to glass, wood pulp, and flax compared to pure PLA. Talc and hemp composites show the weakest TS compared to average values shown by DDGS and high percentage flax (40%). It was noted that increasing filler percentage will usually reduce crystallinity and yield a lower TS for most composites (Huda, 2006). PLA talc (10%) composite(s) shows the greatest FS. Hemp PLA (40%) composites show the weakest values for the each group respectively. Young's modulus accounts for a materials overall stiffness and is the ratio of stress to strain along an axis. Flax (30%-40%) and Glass (40%) composite for PLA drastically increased the YM (GPa) of the plastic material. Wood pulp, hemp, and DDGS show YM values between 1-2 GPa range and retrieved similar properties in this ratio. It should be noted that higher filler percentages showed an inverse relationship with YM values. Elongation at break, or fracture strain, is the ratio comparing changed length and the initial length after failure has occurred. Talc filler was shown to elongate between 30%-70% between filler percentages in PLA composites. DDGS filler was shown to increase PLA EaB by a significant amount as well. If filler percentages become too high plastic to filler bonds decrease, thus, high decreases in EaB can be observed. From a general perspective, PLA was strengthened considerably by glass, flax, wood pulp, and high percentage talc (40%), but most bio-based fillers were observed to decrease overall PLA strength due to relatively weaker bonds. Therefore, it may be beneficial to use filler/plastic bond enhancer for PLA composites. Utilizing the mechanical properties, economic, and life cycle impact data produced in this study, compatible applications for PLA composites may be determined. For example, DDGS and hemp filled composites are relatively inexpensive to produce and maintain a high degree of strength and stress resistance, these specific fillers are recommended for strengthening and reinforcement applications, such as filler in plastic pipping or dynamic joints.

Conclusion

It is shown for both PLA composites that utilization of bio fillers is the more sustainable and economical method of production. Also, the use of organic fillers relinquishes many increases in environmental burdens which can be contributed to inorganic filler composite production. This is due to the ability to receive benefits from landfill and recycling end of life options, when utilizing organic bio fillers. Glass filler is consequently higher in both environmental impact category generation and energy intensity, while DDGS, wood, and rice husks maintain a relatively low environmental impact. Additionally, DDGS and hemp are shown to be the strongest most resistant fillers analyzed. Therefore, not only are bio-filled composites shown to produce lower economic and environmental impact, but also are shown to have comparable or better performance with standard petro-based composites. The effects described in this study are only relative to PLA. Looking ahead, producing this model on different plastic composites such as PHA/PHB, polypropylene, and polyethylene (to name a few) may result in new findings. Additionally, utilization of statistical multivariate analysis to produce an in-depth analysis and test possible hidden interactions between variables and processing parameters would appear to be beneficial to this modeling process.

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Table 2.1. Plastic Comparator model overall assumption list

Step 1: Material Cost/Emission Data

Users may define material composition, including fillers and additives. If material usage, over the production run, is known, the absolute energy usage, cost, and greenhouse emissions will be calculated.

General Settings (user defined):

- Material amount [kg] = **100,000**
- Electricity Cost [$/kWh] = **0.08**
- Fuel Average Admissions [$kgCO_2$/MWh] = **825**

Material Properties (may be user defined):

- Heat Capacity [kJ/kgk] = **1.48**
- Melt Temp. [°c] = **230**
- Base Cost [$/kg] = **3.12**
- Heat Value of Material [MJ/kg] = **43**

Material Acquisition, Monomer Production, and Polymerization (may be user defined):

- Energy Consumed [MJ/kg] = **31**
- Emissions Produced [$kgCO_2$/kg] = **5**

Step 2: Processing Cost/Emission Data

The user may define the injection molding process. This entails the weight and runners associated with the product. Part weight is defined by shot weight divided by the number of cavities. Maintenance cost is defined as a percentage of the injection molding capitol cost. The user will also have to define the operator and overhead costs based from depreciation.

Amount (user defined):

- Part Weight [kg] = **0.01, 0.1, 1**

General Settings (user defined):

- Factor for Transportation of Machine [%] = **0.2**

Injection Molding Machine (user defined):

- Price [$] = **400,000**
- Depreciation Period [yr] = **5**
- Working Hours [hr/yr] = **2,200**
- Cycle Time [s] = **12**
- Process Yield [%] = **85**
- Machine Efficiency [dec.] = **0.6**
- Maintenance Cost [%] = **4**

Labor, Overhead of Injection Molding Machine (user defined):

- Hourly Wage 1 [$/hr] = **25**
- Hourly Wage 2 [$/hr] = **25**

Table 2.1. (Continued)

- Overhead 1 [$] = **1,000**
- Overhead 2 [$] = **500**

Tool, Price to Make Mold (user defined):

- Price [$] = **50,000**
- Maintenance Costs [%] = **2**
- Cavities = **4**

Step 3: Cost Comparison
The cost to manufacture the product from two different plastic materials is compared using a graph as a function of number of parts produced. The price of the material may be user defined or taken from the database. Comparison is generated with the data of costs per part on Y axis and number of parts on X axis.

Step 4: End of Product Treatment
The user may define the end of life scenario for the product. The material may be fragmented into recycling, incineration, or landfill categories. Since many prices are described in wide ranges, the user has the option to define these variables. Once the parameters are set in place, energy, cost, and emissions are generated.
Fragmentation of Material (user defined):

- Recycling [%] = **100**
- Incineration [%] = **100**
- Landfill [%] = **100**

Recycling (user defined):

- Recycling Factor [dec.] = **0.3**

Incineration (user defined):

- Incineration Efficiency [dec.] = **0.5**
- Emissions During Incineration [$kgCO_2/kg$] = **3.11**

Landfill

- Landfill Costs [$/kg] = **0.24**

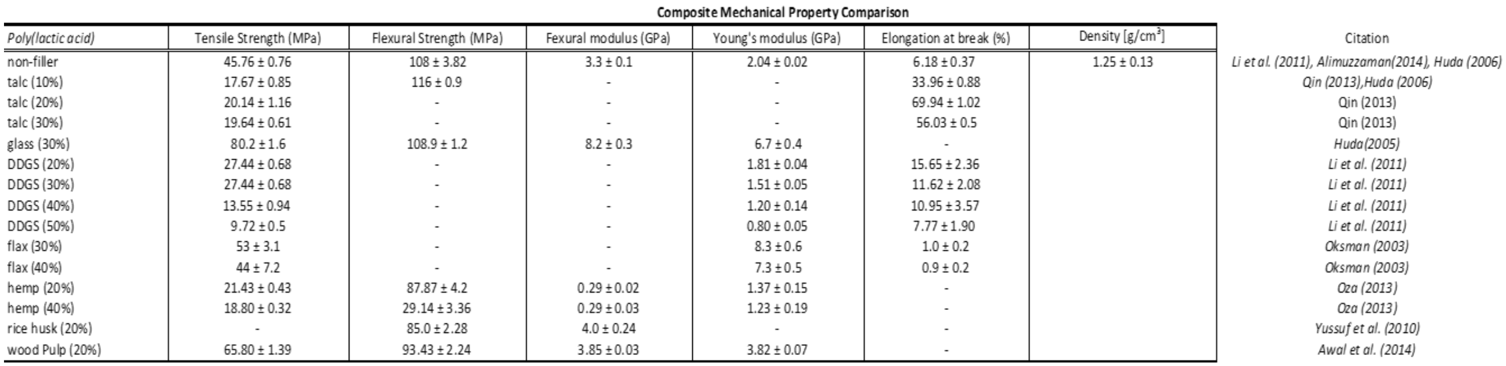
Landfill with Methane Recovery

- Energy Recovery [MJ/kg] = **0.21**
- Financial Benefit [$/kg] = **0.0037**

Table 2.2. Total production cost of material relative to part weight and end-of-life treatment

Material Cost Data								
	0.01 kg	Glass	Talc	DDGS	Flax	Hemp	Rice Husks	Wood
Recycling								
	PLA ($/kg)	9	8.8	8.68	8.78	8.77	8.71	8.68
Incineration								
	PLA ($/kg)	10.4	9.95	9.65	9.9	9.87	9.73	9.64
Landfill								
	PLA ($/kg)	10.8	10.3	10	10.3	10.2	10.1	10
Landfill + Methane								
	PLA ($/kg)	10.6	10.3	9.82	10.1	10	9.9	9.81
No End of Life								
	PLA ($/kg)	10.6	10.1	9.82	10.1	10	9.91	9.82
	0.1 kg	Glass	Talc	DDGS	Flax	Hemp	Rice Husks	Wood
Recycling								
	PLA ($/kg)	2.41	2.22	2.09	2.2	2.18	2.13	2.09
Incineration								
	PLA ($/kg)	3.84	3.37	3.06	3.32	3.28	3.13	3.06
Landfill								
	PLA ($/kg)	4.22	3.74	3.44	3.7	3.66	3.52	3.43
Landfill + Methane								
	PLA ($/kg)	4.01	3.54	3.23	3.49	3.45	3.32	3.23
No End of Life								
	PLA ($/kg)	4.02	3.54	3.23	3.49	3.46	3.32	3.23
	1 kg	Glass	Talc	DDGS	Flax	Hemp	Rice Husks	Wood
Recycling								
	PLA ($/kg)	1.75	1.56	1.43	1.54	1.52	1.47	1.43
Incineration								
	PLA ($/kg)	3.18	2.71	2.4	2.66	2.62	2.49	2.4
Landfill								
	PLA ($/kg)	3.56	3.09	2.78	3.04	3	2.86	2.78
Landfill + Methane								
	PLA ($/kg)	3.35	2.88	2.57	2.83	2.79	2.66	2.57
No End of Life								
	PLA ($/kg)	3.36	2.88	2.57	2.83	2.8	2.66	2.57

Table 2.3. Mechanical properties of poly(lactic acid) composites



Composite Mechanical Property Comparison

Poly(lactic acid)	Tensile Strength (MPa)	Flexural Strength (MPa)	Fexural modulus (GPa)	Young's modulus (GPa)	Elongation at break (%)	Density [g/cm^3]	Citation
non-filler	45.76 ± 0.76	108 ± 3.82	3.3 ± 0.1	2.04 ± 0.02	6.18 ± 0.37	1.25 ± 0.13	*Li et al. (2011), Alimuzzaman(2014), Huda (2006)*
talc (10%)	17.67 ± 0.85	116 ± 0.9	-	-	33.96 ± 0.88		*Qin (2013),Huda (2006)*
talc (20%)	20.14 ± 1.16	-	-	-	69.94 ± 1.02		Qin (2013)
talc (30%)	19.64 ± 0.61	-	-	-	56.03 ± 0.5		Qin (2013)
glass (30%)	80.2 ± 1.6	108.9 ± 1.2	8.2 ± 0.3	6.7 ± 0.4	-		*Huda(2005)*
DDGS (20%)	27.44 ± 0.68	-	-	1.81 ± 0.04	15.65 ± 2.36		*Li et al. (2011)*
DDGS (30%)	27.44 ± 0.68	-	-	1.51 ± 0.05	11.62 ± 2.08		*Li et al. (2011)*
DDGS (40%)	13.55 ± 0.94	-	-	1.20 ± 0.14	10.95 ± 3.57		*Li et al. (2011)*
DDGS (50%)	9.72 ± 0.5	-	-	0.80 ± 0.05	7.77 ± 1.90		*Li et al. (2011)*
flax (30%)	53 ± 3.1	-	-	8.3 ± 0.6	1.0 ± 0.2		*Oksman (2003)*
flax (40%)	44 ± 7.2	-	-	7.3 ± 0.5	0.9 ± 0.2		*Oksman (2003)*
hemp (20%)	21.43 ± 0.43	87.87 ± 4.2	0.29 ± 0.02	1.37 ± 0.15	-		*Oza (2013)*
hemp (40%)	18.80 ± 0.32	29.14 ± 3.36	0.29 ± 0.03	1.23 ± 0.19	-		*Oza (2013)*
rice husk (20%)	-	85.0 ± 2.28	4.0 ± 0.24	-	-		*Yussuf et al. (2010)*
wood Pulp (20%)	65.80 ± 1.39	93.43 ± 2.24	3.85 ± 0.03	3.82 ± 0.07	-		*Awal et al. (2014)*

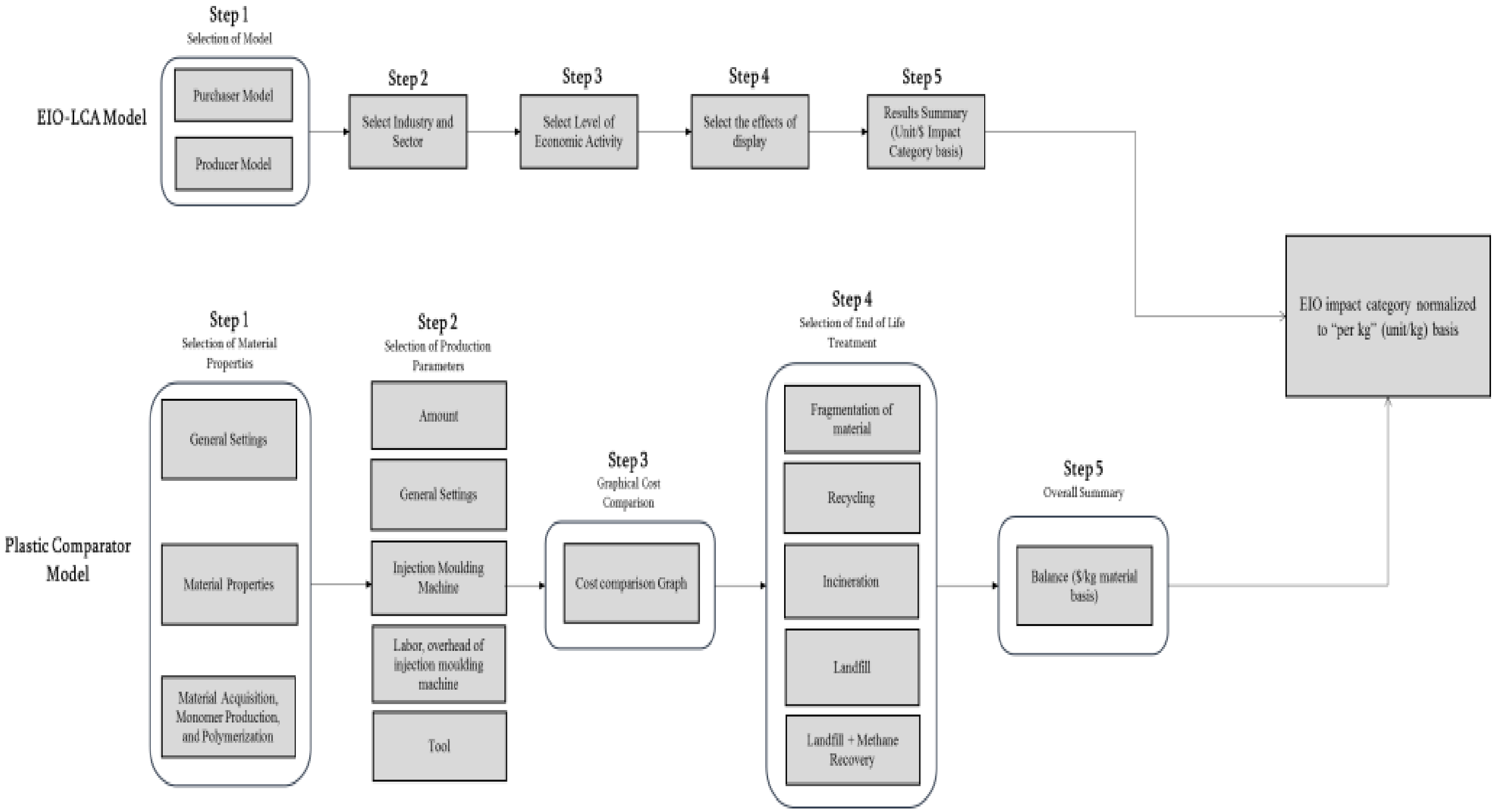


Figure 2.1. Overall methodology process flow chart, EIO-LCA and PC stepwise layout

Figure 2.2. Unit cost [$/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

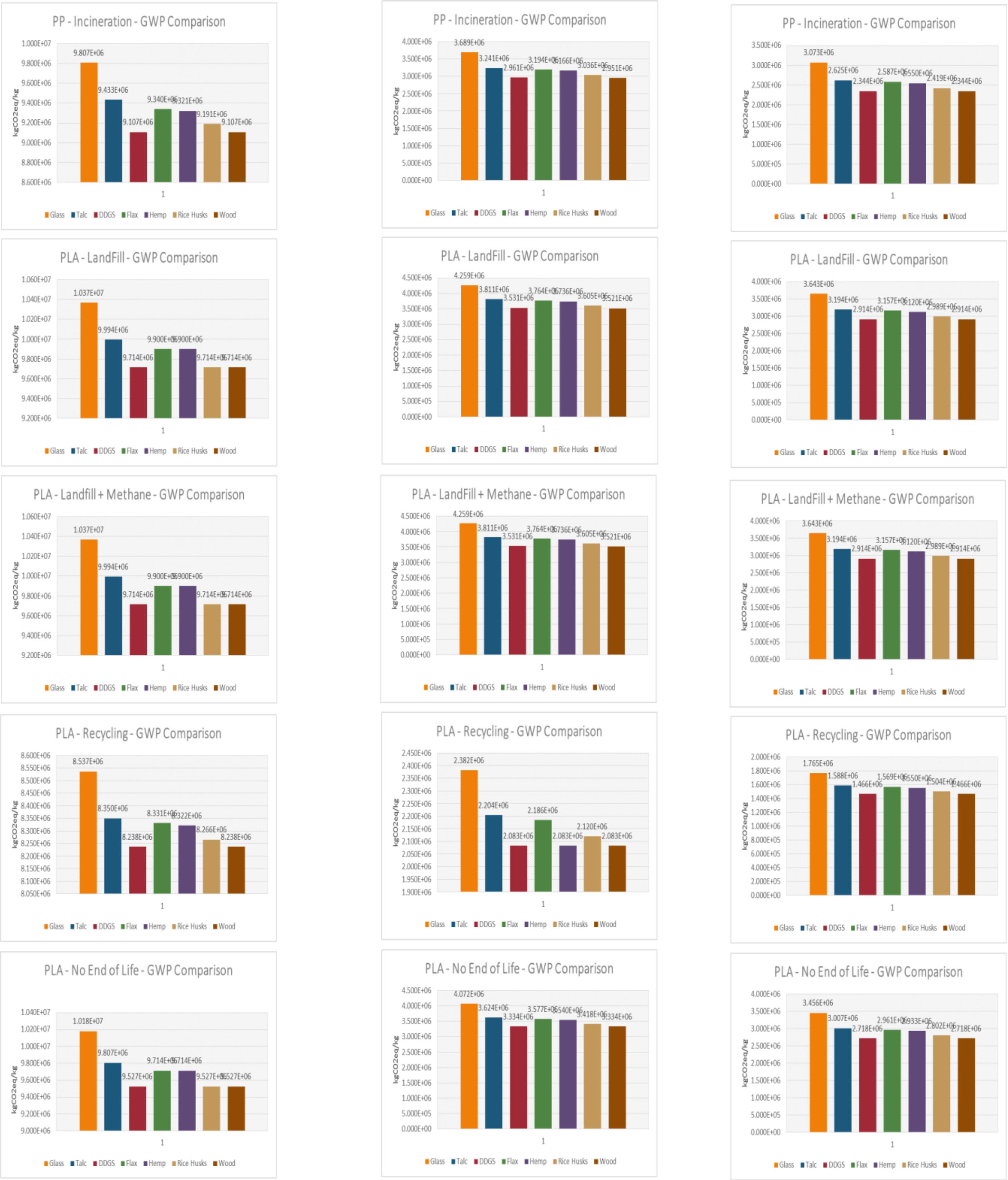


Figure 2.3. GWP [kgCO2eq/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

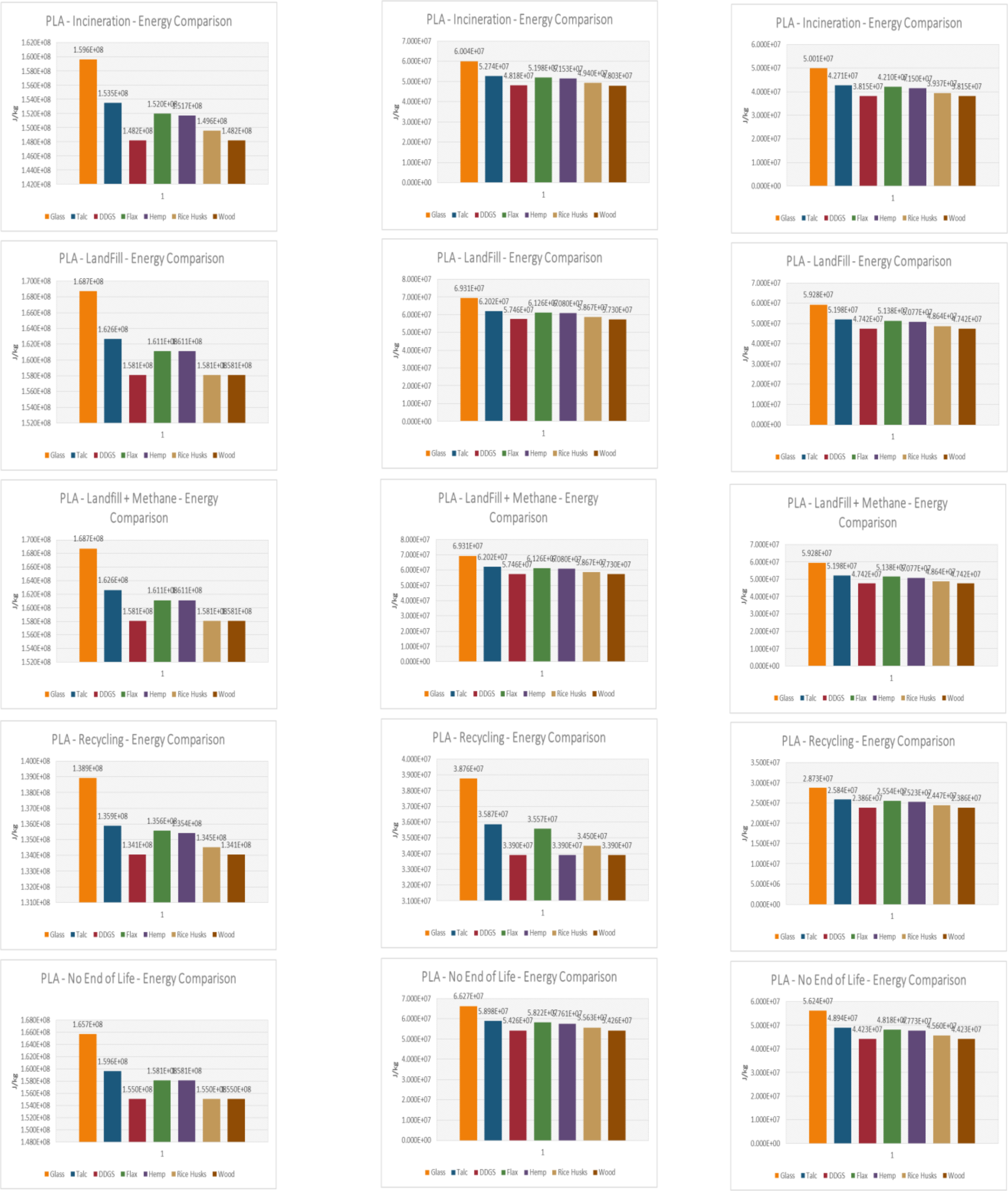


Figure 2.4. Energy Intensity [J/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

Figure 2.5. Air Acidification [kgSO2eq/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

Figure 2.6. Air Eutrophication [kg Ne/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

Figure 2.7. Water Eutrophication [kg Ne/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

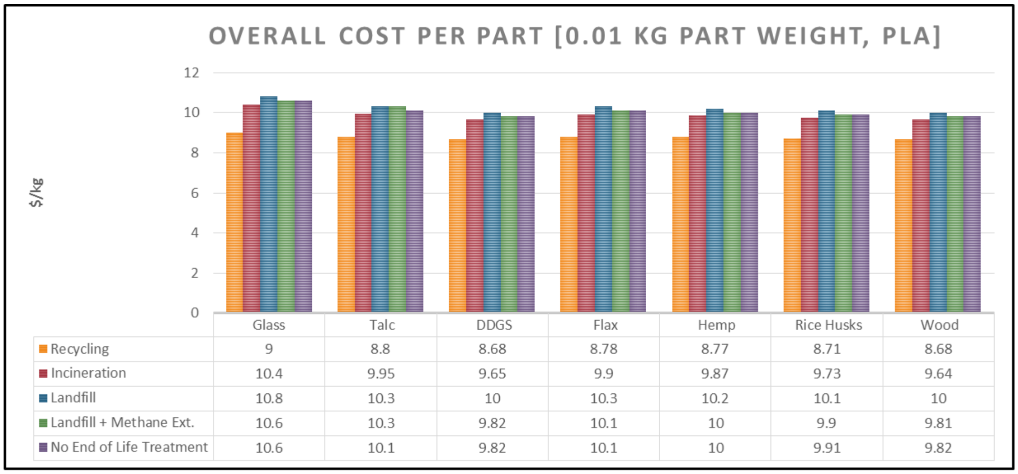
Figure 2.8. Ozone Layer Depletion [kg CFC-11eq/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

Figure 2.9. Air Smog [kg O3/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

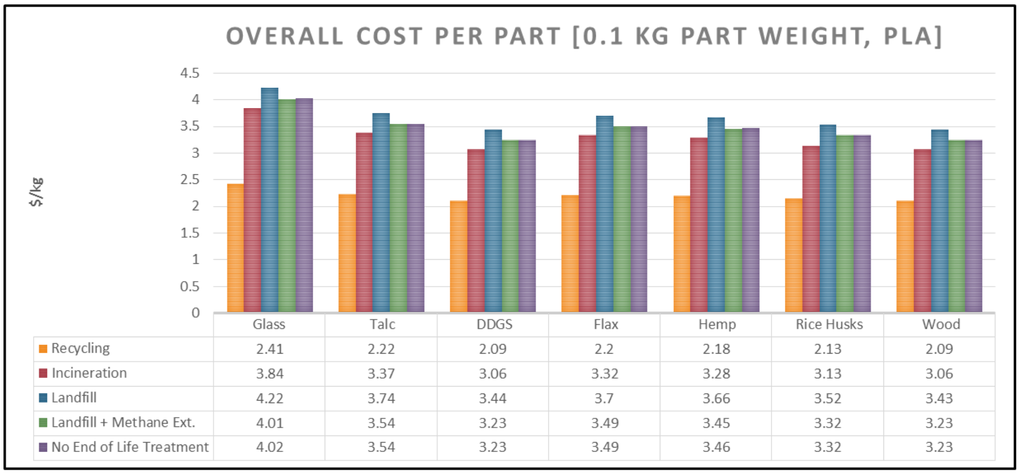
Figure 2.10. High Carcinogen [kg benzene/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

Figure 2.11. High Non-Carcinogen [kg toluene/kg] comparison matrix plots, end of life treatments (I, L, LM, R, N) are compared vertically, while part weight (0.01 kg, 0.1 kg, and 1 kg) is compared horizontally

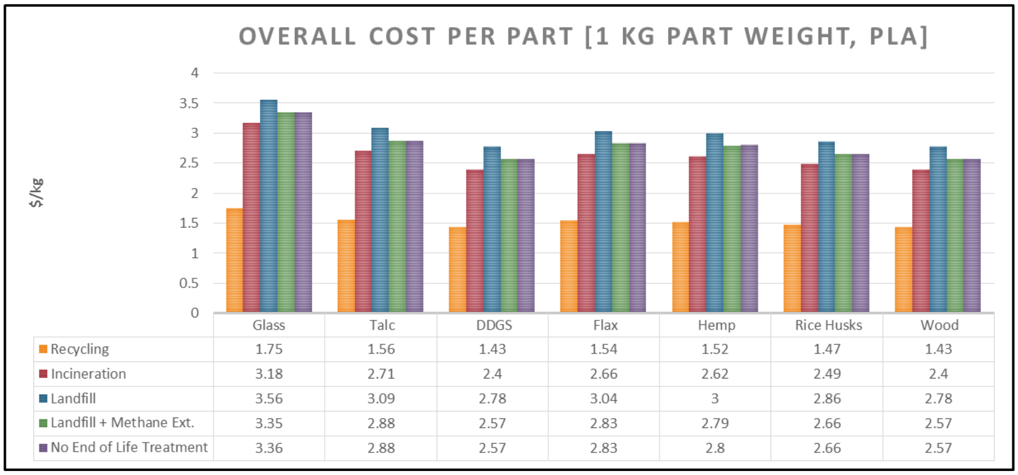
Figure 2.12. Overall processing cost sensitivity analysis. Column 1 is relative to 0.01 kg part weight; column 2 is relative to 0.1 kg part weight; column 3 is relative to 1 kg part weight



	Glass	Talc	DDGS	Flax	Hemp	Rice Husks	Wood
🟧 Recycling	9	8.8	8.68	8.78	8.77	8.71	8.68
🟥 Incineration	10.4	9.95	9.65	9.9	9.87	9.73	9.64
🟦 Landfill	10.8	10.3	10	10.3	10.2	10.1	10
🟩 Landfill + Methane Ext.	10.6	10.3	9.82	10.1	10	9.9	9.81
🟪 No End of Life Treatment	10.6	10.1	9.82	10.1	10	9.91	9.82



	Glass	Talc	DDGS	Flax	Hemp	Rice Husks	Wood
🟧 Recycling	2.41	2.22	2.09	2.2	2.18	2.13	2.09
🟥 Incineration	3.84	3.37	3.06	3.32	3.28	3.13	3.06
🟦 Landfill	4.22	3.74	3.44	3.7	3.66	3.52	3.43
🟩 Landfill + Methane Ext.	4.01	3.54	3.23	3.49	3.45	3.32	3.23
🟪 No End of Life Treatment	4.02	3.54	3.23	3.49	3.46	3.32	3.23



	Glass	Talc	DDGS	Flax	Hemp	Rice Husks	Wood
🟧 Recycling	1.75	1.56	1.43	1.54	1.52	1.47	1.43
🟥 Incineration	3.18	2.71	2.4	2.66	2.62	2.49	2.4
🟦 Landfill	3.56	3.09	2.78	3.04	3	2.86	2.78
🟩 Landfill + Methane Ext.	3.35	2.88	2.57	2.83	2.79	2.66	2.57
🟪 No End of Life Treatment	3.36	2.88	2.57	2.83	2.8	2.66	2.57

Figure 2.13. Overall cost per part compared over filler, end-of-life treatment, and part weight

CHAPTER V:

STATISTICAL CORRELATION AND GROWTH MODELING ANALYSIS OF CROP ROTATION AND NITROGEN APPLICATION EFFECTS ON SOIL CHEMISTRY AND PHYSICAL GROWTH

Abstract

Reducing the environmental footprint of corn production will assure the future sustainability of this important food and industrial crop. Our hypothesis theorized that using new statistical analysis tools, we may observe new correlations, and trends, not originally documented in the initial forgoing study (Riedell, 2009). To test this hypothesis, we statistically correlated corn growth data sets obtained during a two year experiment where corn plots under long-term crop rotation treatments [continuous corn (C-C), corn-soybean rotation (C-S), and corn-soybean-wheat-alfalfa (C-S-G-L)] were treated with fertilizer levels representing high (8.5 Mg ha-1 yield goal) , intermediate (5.3 Mg ha-1), or no N inputs. We developed a linear correlation analysis to investigate soil minerals (N and P), corn growth variables (leaf area, leaf area index, stem length, leaf dry weight, stem dry weight, sheath dry weight, tassel dry weight, and total shoot dry weight), and grain yield interaction trends. Comparing these trends with non-linear growth modeling, we observed unique chemical trends that give insight as to how crop rotation and N application impact our most relevant variables, grain yield and seed starch content. In turn, dynamics between plant essential elements N and P were hypothesized. We conclude that, parallel with the initial study, a combination of legume rotation inclusion, nitrogen application, and soil N and P concentration played an especially significant role in growth changes documented.

Introduction

Corn has proven to be a versatile and important ingredient in food, alcohol, feed, and bio-renewable industries. With the U.S. being one of the world’s agricultural leaders there is a constant ambition to produce crops faster, bigger, and at a higher planting density. To fulfill the world’s food and energy needs, agronomic characteristics of agricultural crops must be fully understood in order to push the boundaries of how much and how fast they can be produced. Many farmers, through experience, have found better yields and soil capacity by diversifying crop rotations and experimenting with nitrogen applications. Crop rotation has been shown to increase growth and yield of corn from year to year. Crop rotations have also been shown to increase potential yields from 2 year, 5 year, and 10 year growth period during Corn-Corn C-C to C-S rotations (Stanger, 2008). During a 12 year study in Northeast Iowa, researchers displayed an average yield of 8.7 MG/ha for rotated corn compared to a 7.7 Mg/ha continuous corn rotation (Karlen, 1985-2003).

The effects of crop rotation have not only resulted better crop yields but an ability to replenish the soil of essential nutrients, such as nitrogen. During a 1984 study (Gass et al.,1984), it was documented that legumes planted in rotation were able to re-furnish the soil with a temporary supply of nitrogen. Nitrogen has been considered as the primary input method for farmers to increase crop growth, but it is also an economically and environmentally expensive nutrient. Thus, many farmers are looking for a cheaper alternative method to increase yields by balancing rotation, nutrients, and planting and harvest periods (Stanger, 2008). Legumes, in rotation, are utilized to increase the soil’s nitrogen carrying capacity and promote root nitrogen uptake. Most increases in yields are due to high legume nitrogen contribution, which can be estimated using a Mitscherlich-Spillman nitrogen response model (Gallagher et al., 2013).

Modeling of corn growth is a desirable utility for many farm and industry based applications due to the high economic incentives an accurate prediction can yield. Modeling may, in turn, effect the management strategies of corn growth over an assortment of weather conditions and environmental changes (Mishoe et al., 1984). A variety of published studies focus modeling efforts on yield variability due to weather and environmental changes (Kiniry, 1996; Pang, 1997a; Jones; 2003; Ritchie, 1990). The CSM-CERES-Maize (CCM) (Kiniry and Jones, 1986) model has garnered world wide application on estimation of corn response to different irrigation and nitrogen application strategies (Cui et al., 2008). The CCM model investigates corn yield response due to environment, genetic interactions and management strategies (Garrison, 1999). In a 1998 study (Paz, 1998) the CSM-CERES model was utilized to optimally select the nitrogen prescription for a desired selection of land by calculating soil temperature, nitrate availability and variable crop growth within the plant and soil environments respectively. While many research endeavors focus on documentation of crop rotation and nitrogen application (Baldock, 1981; Karlen, 1985; Riedell, 2009), there is a lack of research investigating statistic correlation modeling of the effect nitrogen application and corn growth have on overall physical growth and soil chemistry. Our study looks to explore these interactions and document meaningful trends and correlations observed.

The precursor to this study (Riedell, 2009), investigated the nitrogen and crop rotation effects on soil fertility, corn nutrition, yield, and seed characteristics. Nitrogen fertilizer input and crop rotation treatment effects on soil minerals and their effect on shoot dry weight, grain yield and grain composition were investigated over multiple growth seasons in 1998 and 1999. This study documented lower corn shoot nitrogen concentration under C-C and C-S rotations, while under C-S-G-L rotation little to no change in nitrogen concentration was observed due to different initial nitrogen application. Further, through multivariate analysis, many mineral elements, within the shoot, showed nitrogen input x rotation interaction significance. Mineral elements include: P with a P value of 0.05, K with a P value of 0.009, Ca with a P value of 0.006, Mg with a P value of 0.05, and Zn with a P value of 0.005. This study found that soil nitrogen and phosphorus played an especially significant role in corn growth differences observed. The study proposed a combination of nitrogen application, legume rotation inclusion, and legumes providing nitrogen rich substrates for soil nitrogen mineralization led to altered growth effects observed. When N fertilizer was reduced from maximum application to no application, corn growth after a C-C rotation was significantly inhibited. Further, when the same N applications were applied to corn growth after C-S and C-S-G-L the growth altercations were minimal. Last, it was concluded that under a 4 year C-S-G-L rotation the corn grain yield was stable over all nitrogen applications studied, and corn grain yield decreased over all nitrogen applications during C-C monoculture and C-S 2 year rotations.

Through mathematical analysis and quantitative modeling of corn data sets, this study hopes to expand on key aspects of how corn growth responds to crop rotation and nitrogen application, which were first analyzed in the 2009 (Riedell, 2009). By utilizing a new set of computer modeling tools this study hopes to gain new comprehension of the interactions between crop rotation and nitrogen application that effect grain yield and physical growth characteristics. The goal is to answer the following questions; (i) Using the new statistical analysis techniques described, are new trends, or correlations, between the interactions of nitrogen application and crop rotation on corn growth and soil chemistry observed (ii) How do these observed changes in crop growth relate to differences in soil chemistry across different crop rotations and nitrogen inputs? By trying to answer these questions, this study may give useful insight on the impacts crop rotation and nitrogen applications have on corn growth and grain yield.

Materials and Methods

Initial Study

This study analyzes and models the growth of corn under conditions common to the northern U.S. Corn Belt. Initial data, described below, for this project has been previously published (Riedell, 2009). The corn crop was grown at the Eastern South Dakota Soil and Water Research Farm near Brookings, SD (44º 19’ N, 96º 46’ W; 500 m elevation). Starting in 1990, the corn was grown on 3 different crop rotations and replicated three times. These rotations include continuous corn growth (C-C), a 2-year corn to soybean rotation (C-S), and a 4-year corn to soybean to wheat to alfalfa rotation (C-S-G-L). Each plot of corn growth was divided into three subplots and three different nitrogen applications were applied, one relative to each subplot. Nitrogen application rates were based upon yield goals of 0 (low Nitrogen), 5.3 (medium N), and 8.5 (high N) Mg ha-1 (Riedell, 2009). The initial study documented that C-C rotation, high nitrogen application was shown to have the greatest impact on crop yield for all samples (5,000-7,600 kg/ha). Also, medium nitrogen application showed a relatively high impact (5,000-6,800 kg/ha) on grain yield compared to the low nitrogen impact (3,500-4,500 kg/ha), which showed the lowest grain yields of all samples taken. The C-S rotation was shown to have the highest average grain yield for all nitrogen applications, with high and medium nitrogen applications competing for the highest grain yield (6,000-9,000 kg/ha). Low nitrogen application was shown to have the smallest impact (5,200-7,100 kg/ha) but maintained values only relatively lower than the high and medium applications. Observation of the C-S-G-L rotation revealed medium and low nitrogen application as the leading grain yield model (6,000-9,000 kg/ha). High nitrogen application showed the lowest relative values for grain yield (5,000-8,000 kg/ha), supporting a negative correlation between soil nitrogen and grain yield under C-S-G-L shown.

Non-Linear Growth Modeling

The data set contains a large collection of measurements of the corn plant during each rotation and nitrogen application applied. These measurement variables may be viewed on Table 3.1. The modeling procedure began by selecting the measurement variables which quantify a corn plant's physical growth. Modeled variables selected include: leaf area, leaf area index, stem length, leaf dry weight, stem dry weight, sheath dry weight, tassel dry weight, and total shoot dry weight. A quantitative plot model was used to analyze each measured variable over each rotation and nitrogen application. Data points for both years were combined and placed over a common time scale (days 0-220). Once plotted, each variable's data points were fit with an exponential or linear curve and an R^2 value was calculated. The exponential curve was suggested due to the resemblance to the Michaelis-Menten growth function and the high R^2 value associated. There are three graphs for each variable analyzed (Fig. 3.2-3.8), the graphs present growth effects after each nitrogen application and shown over each crop rotation. The three plot approach provides an overall prospective of the independent variable growth effects. The graphic models were compared vertically by crop rotation and horizontally for nitrogen application. Models which maintain discrepancies between linear and exponential trends were fitted with both exponential and linear fit lines. Visual observations were recorded and compared with hypothesis presented in the 2009 study. Relative to each growth data set, exponentially fit equation parameters (a, b) were collected and compared to observe any possible trends relative to different treatments applied, which are shown on Tables 3.2 through 3.8. A compilation of coefficient of determination (R^2) values (Table 3.9) was produced to suggest a proper growth model for each growth parameter. Many curves are shown to fit well, above 0.9, for both linear and exponentially fit curves; this analysis was used to determine which produced the strongest correlation between the two.

Linear Correlation Analysis

To identify the variance of growth effects between rotations and nitrogen applications, correlation tables were made for a direct cross comparison to observe variable relationship and growth impacts. Microsoft Excel 2013 correlation software package was utilized to correlate all variables relative to each nitrogen application and crop rotation treatment applied. To sort through the ample amount of data, Visual Basic (VBA) coding was utilized to produce a linear correlation value heat map between each soil variable (Fig. 3.8). A series of embedded if-then loops were coded to organize the correlation variables into a heat map. The variable heat map was used to compare which plant and soil variables correlate to aid or inhibit the growth and concentration of plant components and mineral elements, and allow for a cross comparison of rotation and nitrogen variable impacts. Each graph, relative to nitrogen application, is placed side by side to visually compare nitrogen effects throughout the growth cycle. To observe the nitrogen and rotation effect on grain yield, a bar plot was developed, which compares each crop rotation through each of the 6 measurement iterations. Each bar graph was developed for nitrogen applications low, medium, and high.

Results and Discussion

Non-Linear Growth Modeling:

Leaf Area, LAI, and Stem Length

Leaf area, LAI, and stem length growth models were shown to be influenced by nitrogen application and crop rotation treatments. Growth curve analysis of the C-C rotation revealed a large impact due to the nitrogen applied as a side dress application at cultivation (Fig. 3.2, Fig. 3.3, Fig. 3.4). The curves suggested the rate of growth was directly related to the amount of nitrogen applied: under the impacts of low nitrogen the highest value measured was obtained near 199-210 days, medium nitrogen near 200-207 days, and high nitrogen near 197-206 days. The highest measured value was shown to increase directly with increasing nitrogen application as well: C-C rotation and low nitrogen application pairing produced the lowest value ranges for all growth variables described above; medium and high nitrogen application produced significantly higher values for all growth characteristics. C-S rotation produced curves with little variation between each nitrogen application. Additionally, the C-S-G-L rotation produced little variation between growth values, and rate of growth, between nitrogen applications and converged to maximum growth in a similar fashion as C-S iterations. Relative to leaf area, LAI, and stem length, high nitrogen application produced the quickest growth, followed by medium, and low. When low amounts of nitrogen were applied, growth was increased, therefore, it was hypothesized that soil maintained a higher nitrogen concentration when crop rotations contained legumes. Therefore, the C-S-G-L and C-S rotations reached a greater area value and converged to the highest maximum value quicker than the C-C rotation. For all applications of nitrogen C-

S-G-L and C-S rotations produced a higher growth value compared to C-C rotation, with exception of a few outlying cases. For exponential and linear fit curves, R^2 values (Table 3.9) were consistently greater than 0.9 for both mathematical functions. The linear fit data showed a stronger coefficient of determination for each rotation and nitrogen application except the C-S-G-L/medium nitrogen pairing, indicating a linear model should be used to describe leaf area growth and LAI. Alternatively, the coefficient of determination was stronger for the exponentially fit curve when describing stem length. A linear model suggested the observed growth trends may have occurred in multiple areas of corn's growth phase for leaf area and LAI. Thus, the growth phase where these observations occurred was deemed inconclusive for these variables.

Dry Weight Variables

Leaf dry weight, stem dry weight, sheath dry weight, and tassel dry weight curves (Fig. 3.5, Fig. 3.6, Fig. 3.7, Fig. 3.8) where observed to have a direct relationship with the amount of nitrogen initially applied: under the impacts of low nitrogen highest measured value was obtained near 203-210 days, medium nitrogen near 200-207 days, and high nitrogen near 198-207 days. The C-C rotation and low nitrogen pairing was shown to produce the lowest weight recorded, while high nitrogen produced the highest amount weight documented. C-S rotation produced curves with little variation between each nitrogen application, and converged to these values in 197.5-203 days, for high, medium, and low nitrogen applications. Moreover, C-S-G-L rotation produced little variation between leaf dry weight values between nitrogen applications. High, medium, and low nitrogen applications produced maximum values within 197-202 days; high and medium applications, nearly identical, produced the quickest growth, followed by low.

For exponential and linear fit curves, R2 values were consistently greater than 0.9 for both mathematical functions. The exponentially fit data showed a stronger coefficient of determination for each rotation and nitrogen, indicating an exponential model should be used to describe weight growth parameters. Therefore, suggesting the growth data documented was relative to the log phase of growth.

Growth Effects

Determination of the growth phase where observations have been documented may indicate valuable data for farmers. Growth stages can be used to help growers make timely applications of herbicides and fungicides (Freeman, 2007). The gathering of coefficient of determination variables (Table 3.9), R^2, suggested that the dry weight parameter growth was documented during the vegetative stage of growth due to the high relation to the exponential curve. Alternatively, leaf area, LAI, and stem length are strongly correlated for both linear and exponentially fit curves, therefore, there is ambiguity as to where the documented growth has occurred. It is hypothesized that the linear growth may have occurred during the inflection point, which occurs at the end of the vegetative phase(s) and into the beginning of the reproduction phase(s). The quantitative plot models show many trends between the variable growth effects (Fig. 3.2-3.8). For all data plots where nitrogen application is compared over rotation, the nitrogen effected growth substantially during the C-C rotation. The total growth rate and growth amplitude were both considerably affected when nitrogen application was increased. During the C-S and C-S-G-L crop rotations, the nitrogen applications showed only minimal growth rate effects, and the total growth amplitude showed only minimal changes between nitrogen applications. This is possibly due to the C-C rotation consuming large amounts of nutrients and leaving soil nitrogen at minimal amounts for next year’s crops. Oppositely, the C-S and C-S-G-L crops may utilize the legume plant’s ability to produce nitrogen in their root nodules and in turn replenish the soil with nutrients for the next year’s rotation. These results are supported by the initial study (Riedell, 2009, Fig. 2) as well. In the study, C-S-G-L rotation was shown to produce to the lowest yield under high nitrogen treatment. Further, the C-C and C-S rotations produced the highest yields under high and medium nitrogen treatment, while producing significantly lower yields under low nitrogen input. A 2005 research study (Mallarino, 2005) conducted at Iowa State’s research farm produced similar results; “Crop rotation greatly increased corn yield compared with continuous corn without N or with low N rates, This rotation benefit in addition to N effects probably showed increased yields because of improved soil physical properties and fewer incidences of diseases and pests”. With the increasing concerns of soil degradation with continuous corn rotation, many studies have looked to address the possible use of legume rotations as a soil nutrient replenishing system. The results found are shown to confirm the findings of this study. A 1982 study (Ebelhar et al., 1982) documented similar outcomes; relative to corn growth, legumes were determined to be useful by providing biologically fixed nitrogen into non-legume rotation systems. The corn which was grown on ground covered in legume mulch was shown to produce 2.5 ha^{-1} more grain yield compared to when the plot was covered in corn residue. Additionally, a 1990 study (Fyson and Oaks, 1990) documented that corn inoculated with legume soils gave a 3 to 4 fold increase in growth relative to the controlled greenhouse sample inoculated with low nutrient sandy loam.

Linear Correlation

The initial study (Riedell, 2009) documented soil nitrogen and phosphorus to maintain the largest canonical discriminant power for nitrogen input and crop rotation treatments, through canonical discriminant analysis. Thus, it was hypothesized that inclusion of legumes within rotation treatments likely resulted in providing high nitrogen substrates for soil mineralization as well as altering the levels of phosphorus which may have been extracted into the plant, which in turn effected the growth variances between rotation treatments and nitrogen applications. To substantiate, or further, these theories, the linear correlation analysis (Fig. 3.8) highlighted instances of high correlation between soil mineral nutrients and selected growth characteristics, yield and grain starch content. Over all levels of nitrogen application, soil nitrogen concentration was shown to have a significant negative correlation with yield during the C-S-G-L treatment. Alternatively, soil nitrogen concentration and yield displayed significant positive correlations for both C-C and C-S rotations when low, medium, and high nitrogen application was applied. Almost the exact relationship was shown for phosphorus as well, though, under low nitrogen application the C-C treatment displayed a negative correlation relationship. Grain starch content and soil nitrogen concentration correlation displayed a significant negative relationship was observed for C-C, C-S, and C-S-G-L treatment over all nitrogen application levels. Grain starch content soil phosphorus concentration and revealed a significant negative relationship during the C-S-G-L treatment and low nitrogen application iteration. Interestingly, this analysis expands on the relationships discussed in the 2009 study; the importance of nitrogen and phosphorus soil content was previously discussed while this analysis suggests the importance of where nitrogen and phosphorus were obtained. During the C-S-G-L rotation, soil nitrogen concentration is shown to universally have strong negative correlation with yield and grain starch content. It is likely that the inclusion of additional soil nitrogen may alter, or disrupt, the contribution of nitrogen the legume crop contributes. It is theorized that new applications of nitrogen onto remaining legume components may disrupt the soils natural nitrogen fixation cycle. Thus, limiting the amount of nitrogen uptake to the plant and disrupting growth characteristics. Due to this, researchers have suggested to use legumes to replace a portion of nitrogen application applied during future corn rotations. A 1993 research study (Robinson, 1993) suggested that fertilization of C-C rotations produced a higher soil organic carbon level but increased CO2 emissions into the atmosphere and suggested utilization of rotations with legumes and small grains to sequester full use of fertilization next C-C rotation period. Additionally, a high correlation between soil nitrogen content and oil concentration in the seed was observed under the C-S and C-S-G-L rotation treatments. Variables that show a similar correlation trend to the overall yield included plant dry weight, plant nitrogen content, and the plant’s starch content. Each of these variables showed a strong negative correlation during the C-S and C-S-G-L rotations for each nitrogen application. The C-C rotation surprisingly showed neither high nor low correlations for oil, yield, or plant dry weight due to soil nitrogen content for each nitrogen application. This was unexpected since corn grown under the C-C rotation had a direct relationship with nitrogen applied (Fig. 3.2). The C-C rotation may be indirectly effected by the impact nitrogen application plays on the other soil chemicals such as nitrogen and phosphorus. It was found that other related studies have produced similar results. A 1998 study (Eghball and Power, 1998) investigated the effects of P and N soil content on corn yield. The study found that both P and N had increased grain yield and that both had similar effects on the grain yield for each of the 4 years tested. Additionally, a 2005 study (Warman and Termeer, 2005) investigated the concentration of N, P, and K in sewage sludge, and documented the effects implementation of sewage sludge as corn fertilizer. During this investigation it was documented that all three nutrient parameters had a positive correlation with corn yield.

Conclusion

The most important findings for this study are observed in the developed correlation analysis and non-linear growth models. The trends observed support the previous research study and maintain that there are significant variances in growth characteristics occurring not only due to nitrogen application and crop rotation, but also due to how soil obtains nitrogen and phosphorus. Over the 2 years' worth of growth data, nitrogen applications were shown to effect growth over all crop rotations. The nitrogen applied during the C-C rotation showed the greatest increase in growth amplitude and speed. During the C-S rotation the nitrogen showed a similar effect as applied to the C-C rotation, but the overall effect was not as great. Nitrogen applications during the C-S-G-L rotations were shown to have the least effect overall. For most plots observed, the C-S-G-L responded by a slight increase in growth during a high nitrogen application, but the mid to low nitrogen applications had produced minimal effects. Overall, the C-S rotation shows the most efficient grain yield production, but also uses higher nitrogen applications to achieve these values. C-C rotation was observed to need high nitrogen applications to get mid-range grain yield values (5000-7600 kg/ha). C-S-G-L rotation receives the highest grain yield values with the smallest use of nitrogen application. The soil linear correlation highlighted the negative effects additional nitrogen applications may have on soil including legume components. The inclusion of legumes as a natural manure source in cropping systems or as a rotation component is shown to positively affect soil properties and increase nitrogen (N) supply; further, P supply is shown to be more prominent within the main crop/following crop (Kabir and Koide, 2002). The plots comparing crop rotations over nitrogen applications show interesting rotational effects. During low nitrogen applications the crop rotations prove to greatly affect the rate and amplitude of the corn growth. The C-S-G-L rotation showed the greatest effect followed by C-S and the least with C-C rotations. The data suggests that the more diverse rotation will increase the corn growth the following year, and may enrich the soil with a unique blend of nutrients which the corn plants can thrive off of. Alternatively, when the corn is continuously planted over a C-C rotation, soil minerals may become expended and poor growth may follow.

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Table 3.1. Variable Introduction

Independent Variables			
Year	Nitrogen Application (applied before growth)	Rotation (CC,CS,CSGL)	

Dependent Variables	**Description**	**Units**	**Abbreviation**
Plant Properties	Plant dry weight	g/plant	pDWg
	Nitrogen content per kg of plant	g/kg	pNgkg
	Phosphorus content per kg of plant	g/kg	pPgkg
	Potassium content per kg of plant	g/kg	pKgkg
	Calcium content per kg of plant	g/kg	pCAgkg
	Magnesium content per kg of plant	g/kg	pMGgkg
	Iron content per kg of plant	mg/kg	pFEmgkg
	Manganese content per kg of plant	mg/kg	pMNmgkg
	Zinc content per kg of plant	mg/kg	pZNmgkg
Grain Properties	Yield	kg/ha	Yieldkgha
	Oil content kg of grain	g/kg	Oilgkg
	Starch content per kg of grain	g/kg	Starchgkg
	Nitrogen content per kg of grain	g/kg	gNgkg
	Phosphorus content per kg of grain	g/kg	gPgkg
	Potassium content per kg of grain	g/kg	gKgkg
	Calcium content per kg of grain	g/kg	gCagkg
	Magnesium content per kg of grain	g/kg	gMggkg
	Iron content per kg of grain	mg/kg	gFemgkg
	Manganese content per kg of grain	mg/kg	gMnmgkg
	Zinc content per kg of grain	mg/kg	gZnmgkg
	Sulfur content per kg of grain	g/kg	gSgkg
Soil Properties	NO3 content per kg of soil	mg/kg	sNO3mgkg
	Phosphorus per kg of soil	mg/kg	sPmgkg
	Potassium content per kg of soil	mg/kg	SKmgkg
	Calcium content per kg of soil	mg/kg	sCamgkg
	Magnesium content per kg of soil	mg/kg	sMgmgkg
	Iron content per kg of soil	mg/kg	sFemgkg
	Manganese content per kg of soil	mg/kg	sMnmgkg
	Zinc content per kg of soil	mg/kg	sZnmgkg

Dependent Variables	**Description**	**Units**	**Abbreviation**
	Protein	g/kg	-
	Oil	g/kg	-
	Starch	g/kg	-
	B	mg/kg	-
	Ca	g/kg	-
	Fe	mg/kg	-
	K	g/kg	-
	Mg	g/kg	-
	Mn	mg/kg	-
	Na	g/kg	-
	P	g/kg	-
	S	g/kg	-
	Zn	mg/kg	-
	Leaf Area	cm^2/plant	leafarea
	Leaf Area Index	-	Lai
	Stem Length	cm/plant	stemleng
Total Weight Properties:	Leaf Dry Weight	g/plant	leafdw
	Stem Dry Weight	g/plant	stemdw
	Sheath Dry Weight	g/plant	sheathdw
	Tassel Dry Weight	g/plant	tasseldw
	Ear Dry Weight	g/plant	eardw
	Total Shoot Dry Weight	g/plant	totshootdw
Leaf Properties:	Nitrogen content	Percentage	Lnpercent
	Phosphorus content	Percentage	Lppercent
	Potassium content	Percentage	Lkpercent
	Sulfur content	Percentage	Lspercent
	Calcium content	Percentage	Lcapercent
	Magnesium content	Percentage	Lmgpercent
	Zinc content	µZn/Zn	Lznppm
	Iron content	µFe/Fe	Lfeppm
	Manganese content	µMn/Mn	Lmnppm
	Copper content	µCu/Cu	Lcuppm
Sheath Properties:	Nitrogen content	Percentage	SHnpercent
	Phosphorus content	Percentage	SHppercent
	Potassium content	Percentage	SHkpercent
	Sulfur content	Percentage	SHspercent
	Calcium content	Percentage	SHcapercent
	Magnesium content	Percentage	SHmgpercent
	Zinc content	µZn/Zn	SHznppm
	Iron content	µFe/Fe	SHfeppm
	Manganese content	µMn/Mn	SHmnppm
	Copper content	µCu/Cu	sHcuppm
Stem Properties	Nitrogen content	Percentage	STnpercent

	Phosphorus content	Percentage	STppercent
	Potassium content	Percentage	STkpercent
	Sulfur content	Percentage	STspercent
	Calcium content	Percentage	STcapercent
	Magnesium content	Percentage	STmgpercent
	Zinc content	µZn/Zn	STznppm
	Iron content	µFe/Fe	STfeppm
	Manganese content	µMn/Mn	STmnppm
	Copper content	µCu/Cu	STcuppm
Tassel Properties:	Nitrogen content	Percentage	Tnpercent
	Phosphorus content	Percentage	Tppercent
	Potassium content	Percentage	Tkpercent
	Sulfur content	Percentage	Tspercent
	Calcium content	Percentage	Tscapercent
	Magnesium content	Percentage	Tmgpercent
	Zinc content	µZn/Zn	Tznppm
	Iron content	µFe/Fe	Tfeppm
	Manganese content	µMn/Mn	Tmnppm
	Copper content	µCu/Cu	Tcuppm
Ear Properties:	Nitrogen content	Percentage	Enpercent
	Phosphorus content	Percentage	Eppercent
	Potassium content	Percentage	Ekpercent
	Sulfur content	Percentage	Espercent
	Calcium content	Percentage	Ecapercent
	Magnesium content	Percentage	Emgpercent
	Zinc content	µZn/Zn	Eznppm
	Iron content	µFe/Fe	Efeppm
	Manganese content	µMn/Mn	Enppm
	Copper content	µCu/Cu	Ecuppm

Table 3.2. Regression parameters for leaf area, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
		Nitrogen Application				Nitrogen Application				Nitrogen Application		
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	0.0424	0.0415	0.0361		0.0567	0.0583	0.0598		0.8983	0.9304	0.9406
	C-S	0.0139	0.0197	0.0364		0.0646	0.063	0.06		0.922	0.9559	0.914
	C-S-G-L	0.0257	0.0146	0.0195		0.0621	0.0654	0.0641		0.9423	0.9358	0.9396
2	C-C	4.24E-02	4.15E-02	3.61E-02		0.0569	0.0583	0.0598		0.8983	0.9304	0.9406
	C-S	1.39E-02	3.64E-02	1.97E-02		0.646	0.06	0.063		0.922	0.914	0.9559
	C-S-G-L	2.57E-02	1.46E-02	1.95E-02		0.621	0.0654	0.0641		0.9423	0.9358	0.9396

Table 3.3. Regression parameters for leaf area index, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
		Nitrogen Application				Nitrogen Application				Nitrogen Application		
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	0.00002	0.00002	0.00002		0.0571	0.0589	0.06		0.8307	0.9486	0.9311
	C-S	0.000008	0.00002	0.00001		0.0645	0.0605	0.063		0.9045	0.9302	0.9418
	C-S-G-L	0.00005	0.00003	0.00002		0.0553	0.0584	0.0615		0.9343	0.923	0.9094
2	C-C	2.00E-05	8.00E-06	5.00E-05		0.0571	0.0645	0.0553		0.8307	0.9045	0.9343
	C-S	2.00E-05	2.00E-05	2.00E-05		0.0589	0.0605	0.0615		0.9486	0.9302	0.9094
	C-S-G-L	2.00E-05	1.00E-05	3.00E-05		0.06	0.063	0.0584		0.9311	0.9418	0.923

Table 3.4. Regression parameters for stem length, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
		Nitrogen Application				Nitrogen Application				Nitrogen Application		
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	0.000005	0.00000004	0.00000002		0.1051	0.1084	0.1135		0.9716	0.9845	0.9801
	C-S	0.00000002	0.00000002	0.00000001		0.1131	0.1144	0.1153		0.9828	0.9809	0.9865
	C-S-G-L	0.00000002	0.00000002	0.00000001		0.1129	0.1137	0.1168		0.9857	0.9797	0.9835
2	C-C	5.00E-08	2.00E-08	2.00E-08		0.1051	0.1131	0.1129		0.9716	0.9828	0.9857
	C-S	4.00E-08	2.00E-08	2.00E-08		0.1084	0.1144	0.1137		0.9845	0.9809	0.9797
	C-S-G-L	2.00E-08	1.00E-08	1.00E-08		0.1135	0.1168	0.1168		0.9801	0.9835	0.9835

Table 3.5. Regression parameters for leaf dry weight, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
		Nitrogen Application				Nitrogen Application				Nitrogen Application		
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	0.00003	0.00006	0.00004		0.0668	0.0653	0.068		0.88	0.8944	0.9296
	C-S	0.00002	0.00004	0.00007		0.0728	0.0684	0.0658		0.9134	0.903	0.8901
	C-S-G-L	0.00004	0.00003	0.00002		0.0691	0.0716	0.0731		0.9207	0.9281	0.9215
2	C-C	3.00E-05	2.00E-05	4.00E-05		0.0668	0.0728	0.0691		0.88	0.9134	0.9207
	C-S	6.00E-05	7.00E-05	2.00E-05		0.0653	0.0658	0.0731		0.8944	0.8901	0.9395
	C-S-G-L	4.00E-05	4.00E-05	3.00E-05		0.0684	0.068	0.0716		0.903	0.9296	0.9291

Table 3.6. Regression parameters for stem dry weight, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
			Nitrogen Application				Nitrogen Application				Nitrogen Application	
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	2E-13	5E-13	5E-13		0.1594	0.1568	0.1586		0.9497	0.953	0.9646
	C-S	3E-13	1E-12	2E-13		0.1607	0.1554	0.1646		0.9646	0.9539	0.9563
	C-S-G-L	3E-13	5.00E-14	1.00E-14		0.1622	0.1726	0.1803		0.8585	0.9656	0.9563
2	C-C	2.00E-13	3.00E-13	3.00E-13		0.1594	0.1607	0.1622		0.9497	0.9646	0.9585
	C-S	5.00E-13	1.00E-12	1.00E-14		0.1568	0.1554	0.1803		0.953	0.9539	0.9563
	C-S-G-L	5.00E-13	2.00E-13	5.00E-14		0.1586	0.1646	0.1726		0.9646	0.9563	0.9556

Table 3.7. Regression parameters for sheath dry weight, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
			Nitrogen Application				Nitrogen Application				Nitrogen Application	
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	0.0000002	0.0000006	0.0000005		0.0886	0.0852	0.0874		0.9313	0.9598	0.9655
	C-S	0.0000002	0.0000004	0.0000006		0.091	0.0884	0.0859		0.9596	0.9543	0.9387
	C-S-G-L	5.00E-07	4.00E-07	2.00E-07		0.0869	0.0898	0.0931		0.9563	0.9698	0.9739
2	C-C	2.00E-07	2.00E-07	5.00E-07		0.0886	0.091	0.0869		0.9313	0.9596	0.9563
	C-S	6.00E-07	6.00E-07	2.00E-07		0.0852	0.0859	0.0931		0.9598	0.9387	0.9739
	C-S-G-L	5.00E-07	4.00E-07	4.00E-07		0.0874	0.0884	0.0898		0.9655	0.9543	0.9698

Table 3.8. Regression parameters for tassel dry weight, this is observed over all rotations (C-C, C-S, and C-S-G-L) and applications (High, Med, and Low). A, b, and R^2 values are parameters of the respected fit exponential curve

		A parameter				b parameter				R^2		
		Nitrogen Application				Nitrogen Application				Nitrogen Application		
Figure	Rotation	Low	Medium	High		Low	Medium	High		Low	Medium	High
1	C-C	0.00000002	0.000000007	0.000000006		0.0923	0.0988	0.1008		0.918	0.9471	0.9578
	C-S	0.000000005	0.000000007	0.000000005		0.1007	0.0995	0.1021		0.9184	0.9658	0.9431
	C-S-G-L	8.00E-09	9.00E-09	8.00E-09		0.0991	0.0995	0.1058		0.9433	0.9518	0.9545
2	C-C	2.00E-08	5.00E-09	8.00E-09		0.0923	0.1007	0.0995		0.918	0.9184	0.9604
	C-S	7.00E-09	7.00E-09	3.00E-09		0.0988	0.0995	0.1058		0.9471	0.9658	0.9545
	C-S-G-L	6.00E-09	5.00E-09	9.00E-09		0.1008	0.1021	0.0995		0.9578	0.9431	0.9518

Table 3.9. Coefficient variables for exponentially and linearly fit curves, relative to each physical growth characteristic

Leaf Area (Rotation : Nitrogen)	**R^2 Value (Exponential)**	**R^2 Value (Linear)**	**Stem Dry Weight (Rotation : Nitrogen)**	**R^2 Value (Exponential)**	**R^2 Value (Linear)**
C-C : Low	0.898	0.917	C-C : Low	0.949	-
C-C : Medium	0.93	0.954	C-C : Medium	0.953	-
C-C : High	0.94	0.9736	C-C : High	0.964	-
C-S : Low	0.922	0.954	C-S : Low	0.964	-
C-S : Medium	0.955	0.932	C-S : Medium	0.953	-
C-S : High	0.914	0.98	C-S : High	0.956	-
C-S-G-L : Low	0.942	0.956	C-S-G-L : Low	0.958	-
C-S-G-L : Medium	0.935	0.923	C-S-G-L : Medium	0.965	-
C-S-G-L : High	0.939	0.946	C-S-G-L : High	0.956	-
Leaf Area Index (Rotation : Nitrogen)	**R^2 Value (Exponential)**	**R^2 Value (Linear)**	**Sheath Dry Weight (Rotation : Nitrogen)**	**R^2 Value (Exponential)**	**R^2 Value (Linear)**
C-C : Low	0.83	0.889	C-C : Low	0.931	0.932
C-C : Medium	0.948	0.944	C-C : Medium	0.959	0.931
C-C : High	0.931	0.96	C-C : High	0.965	0.929
C-S : Low	0.904	0.927	C-S : Low	0.959	0.894
C-S : Medium	0.92	0.951	C-S : Medium	0.954	0.934
C-S : High	0.941	0.969	C-S : High	0.938	0.892
C-S-G-L : Low	0.934	0.931	C-S-G-L : Low	0.956	0.906
C-S-G-L : Medium	0.923	0.921	C-S-G-L : Medium	0.969	0.933
C-S-G-L : High	0.909	0.937	C-S-G-L : High	0.973	0.941
Stem Length (Rotation : Nitrogen)	**R^2 Value (Exponential)**	**R^2 Value (Linear)**	**Sheath Dry Weight (Rotation : Nitrogen)**	**R^2 Value (Exponential)**	**R^2 Value (Linear)**
C-C : Low	0.971	0.796	C-C : Low	0.918	-
C-C : Medium	0.984	0.827	C-C : Medium	0.947	-
C-C : High	0.98	0.867	C-C : High	0.957	-
C-S : Low	0.982	0.837	C-S : Low	0.918	-
C-S : Medium	0.98	0.852	C-S : Medium	0.965	-
C-S : High	0.986	0.858	C-S : High	0.943	-
C-S-G-L : Low	0.985	0.852	C-S-G-L : Low	0.943	-
C-S-G-L : Medium	0.979	0.855	C-S-G-L : Medium	0.951	-
C-S-G-L : High	0.983	0.833	C-S-G-L : High	0.954	-
Leaf Dry Weight (Rotation : Nitrogen)	**R^2 Value (Exponential)**	**R^2 Value (Linear)**			
C-C : Low	0.88	-			
C-C : Medium	0.894	-			
C-C : High	0.929	-			
C-S : Low	0.913	-			
C-S : Medium	0.903	-			
C-S : High	0.89	-			
C-S-G-L : Low	0.92	-			
C-S-G-L : Medium	0.929	-			
C-S-G-L : High	0.931	-			

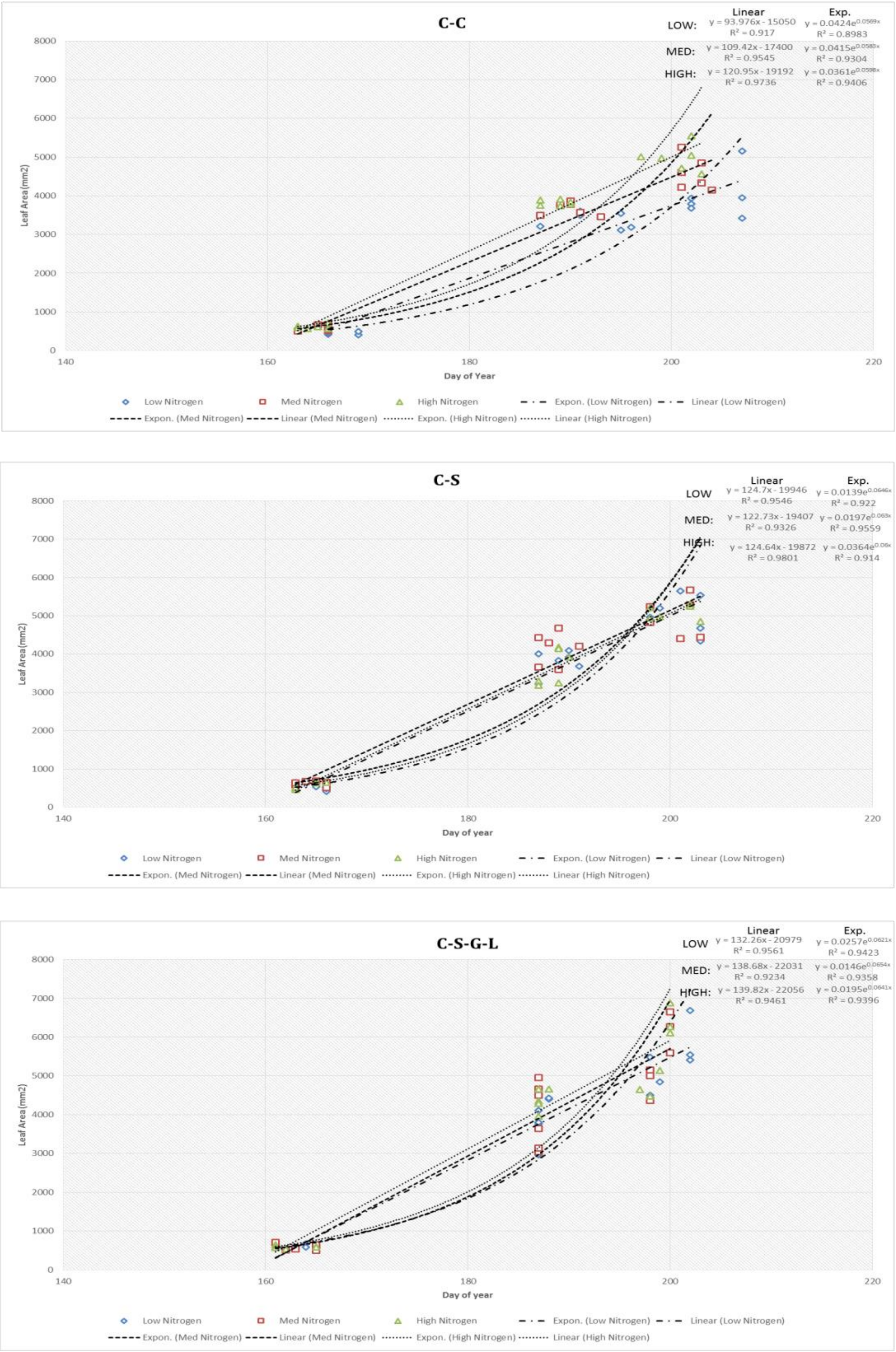

Figure 3.1. Effects of nitrogen application (High, Med, and Low) over time on leaf area for each crop rotation (C-C, C-S, and C-S-G-L) (R^2: Linear on left, exponential on right)

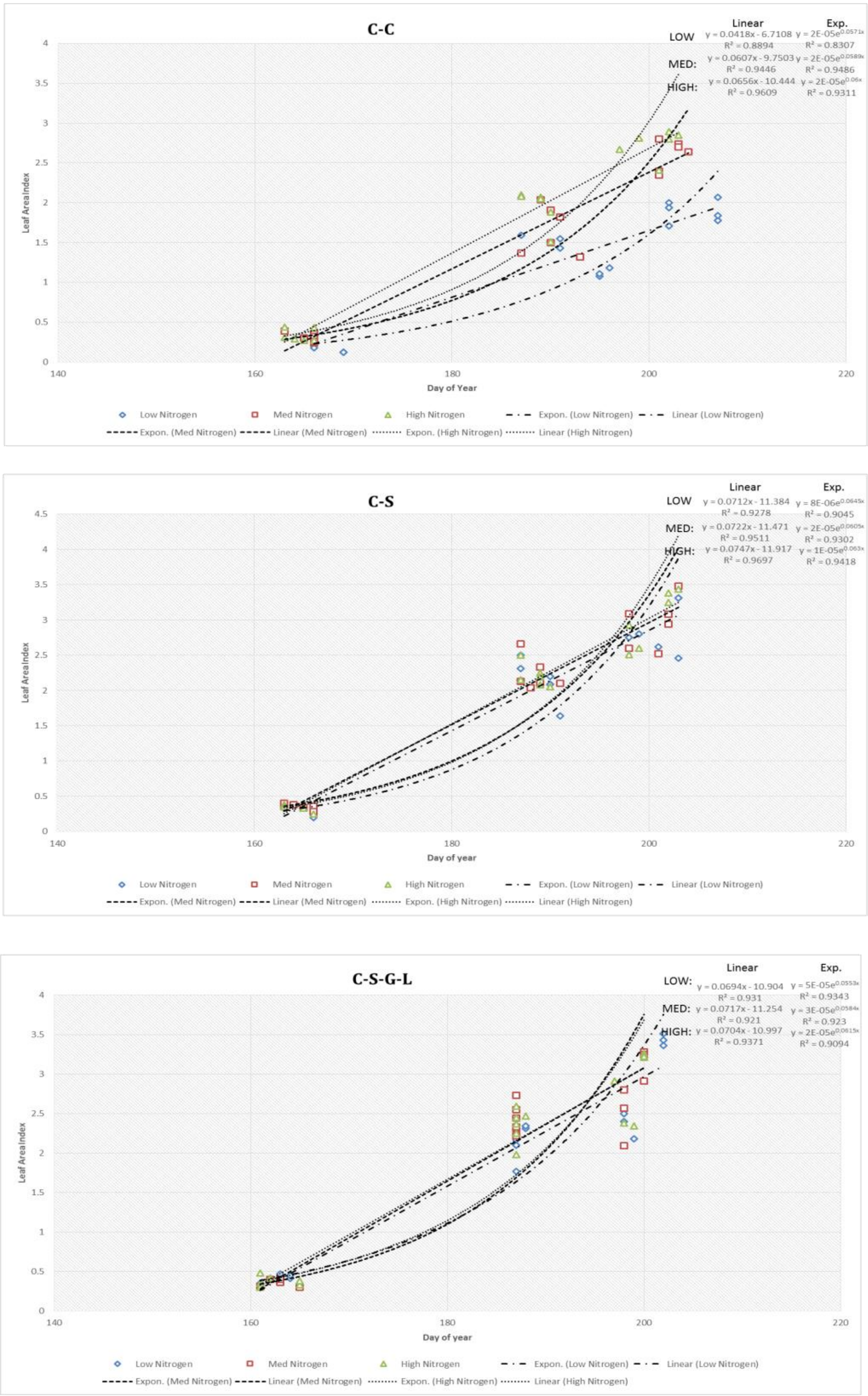

Figure 3.2. Effects of nitrogen (High, Med, and Low) over time on leaf area index for each crop rotation (C-C, C-S, and C-S-G-L) (R^2: Linear on left, exponential on right)

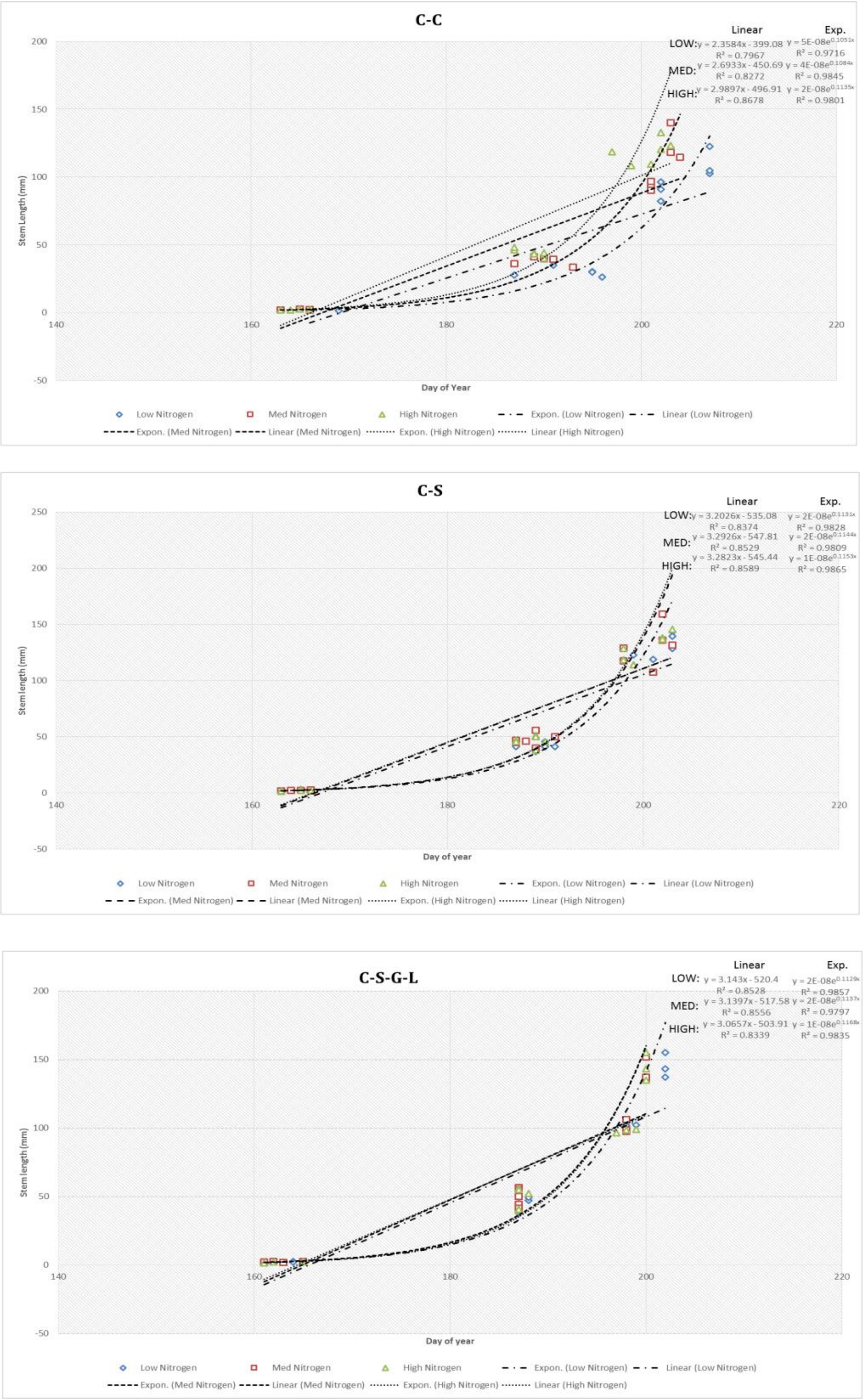

Figure 3.3. Effects of nitrogen application (High, Med, and Low) over time on stem length for each crop rotation (C-C, C-S, and C-S-G-L) (R^2: Linear on left, exponential on right)

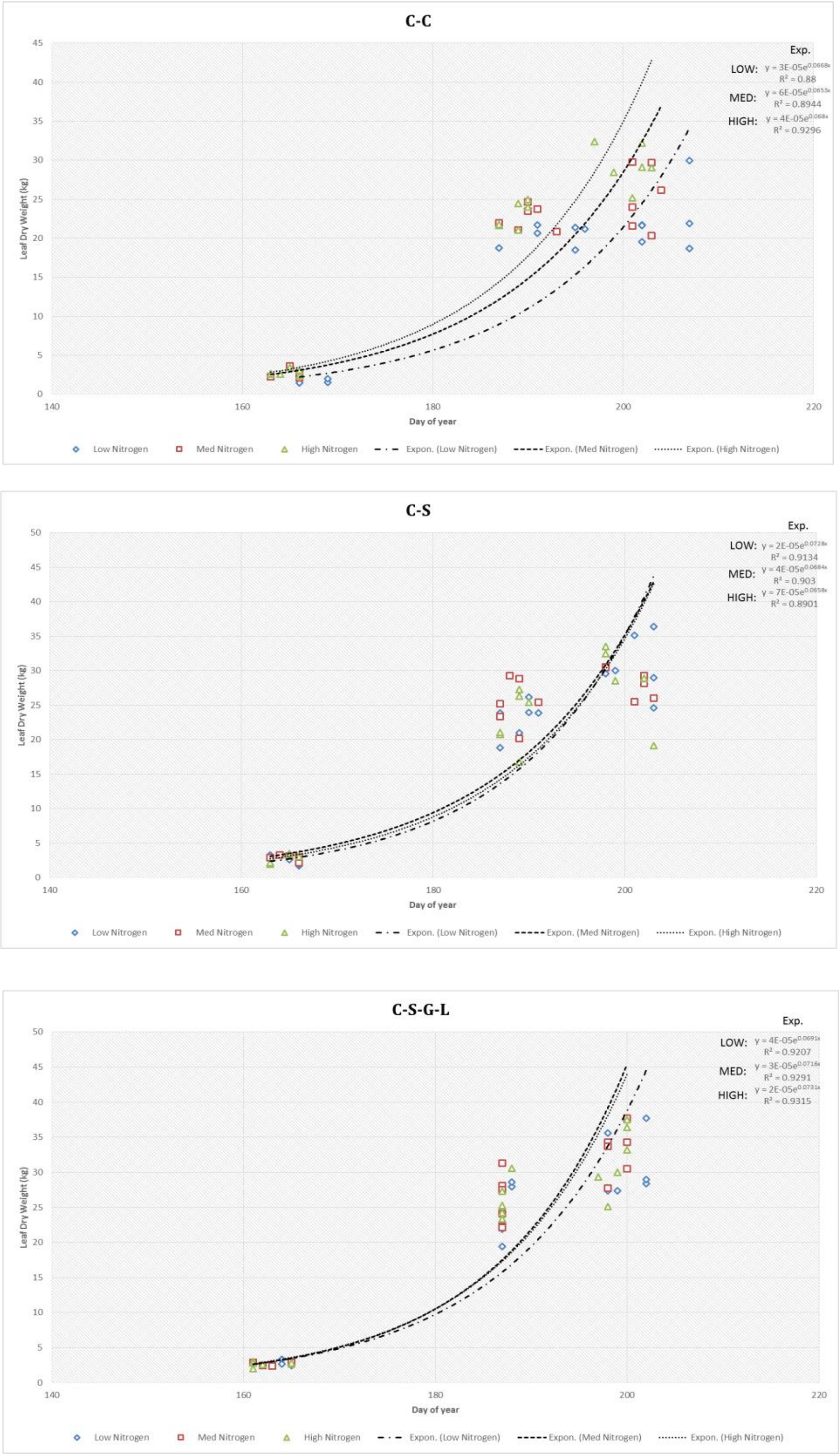

Figure 3.4. Effects of nitrogen application (High, Med, and Low) over time on leaf dry weight for each crop rotation (C-C, C-S, and C-S-G-L)

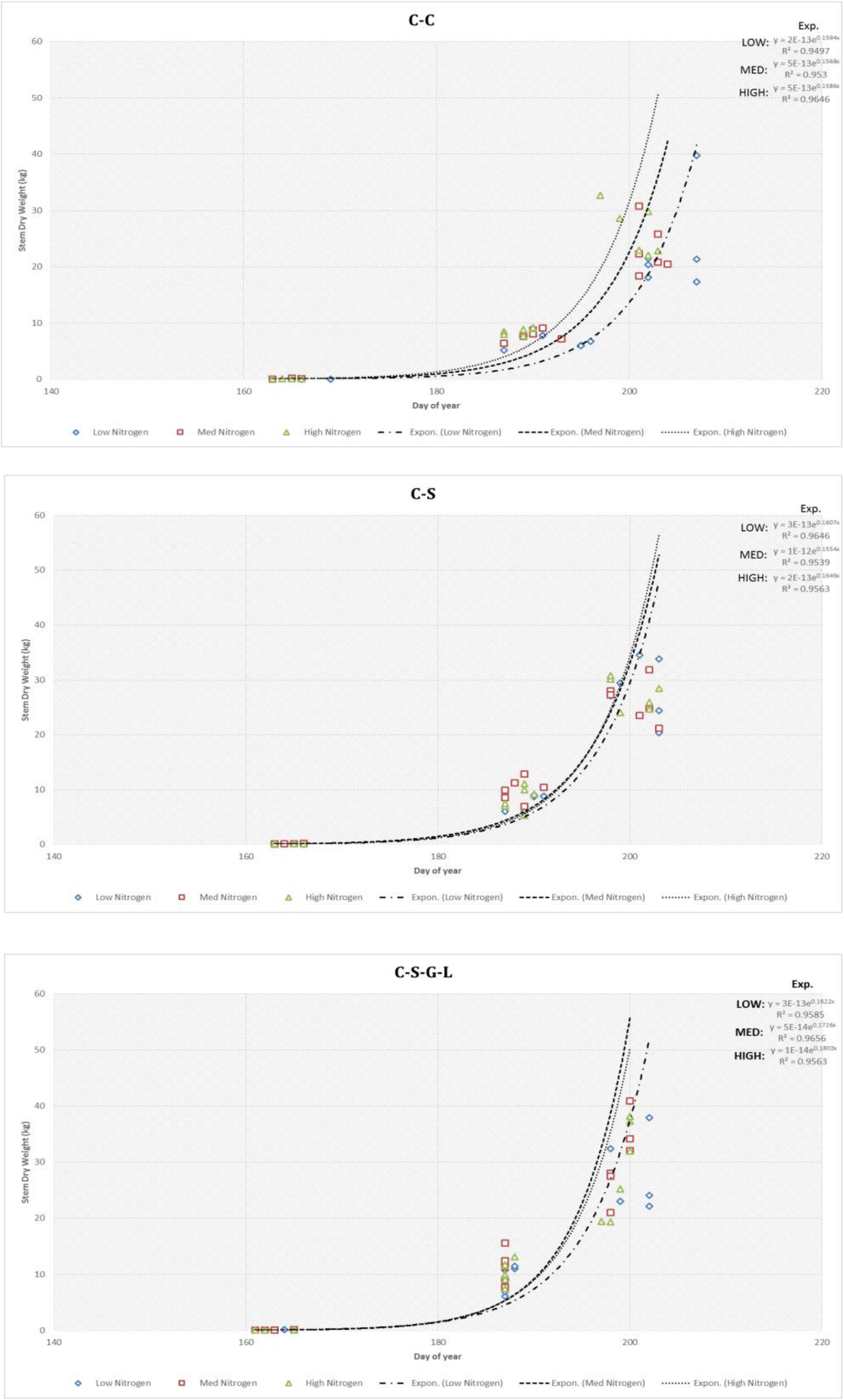

Figure 3.5. Effects of nitrogen application (High, Med, and Low) over time on stem dry weight for each crop rotation (C-C, C-S, and C-S-G-L)

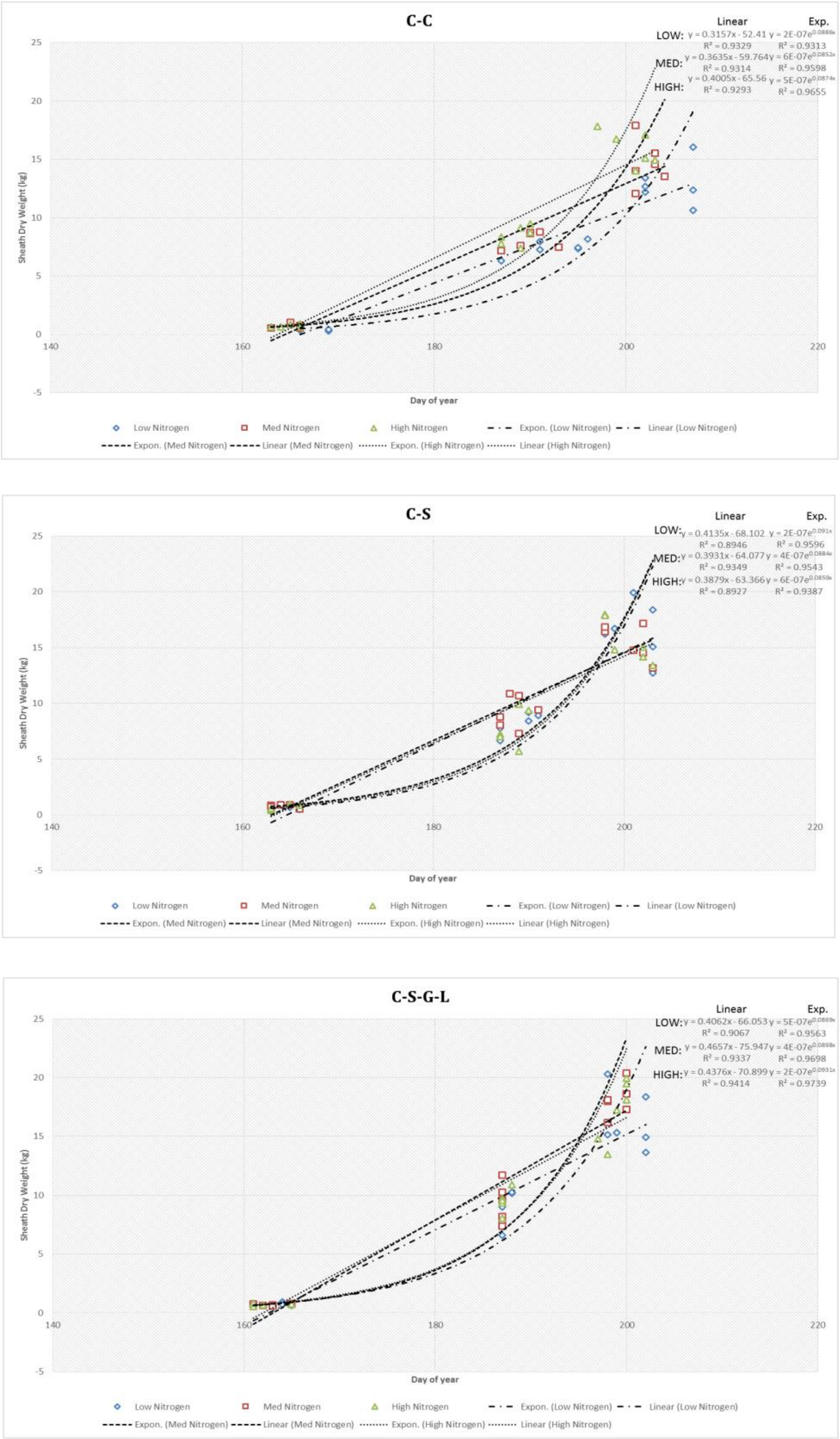

Figure 3.6. Effects of nitrogen application (High, Med, and Low) over time on sheath dry weight for each crop rotation (C-C, C-S, and C-S-G-L)

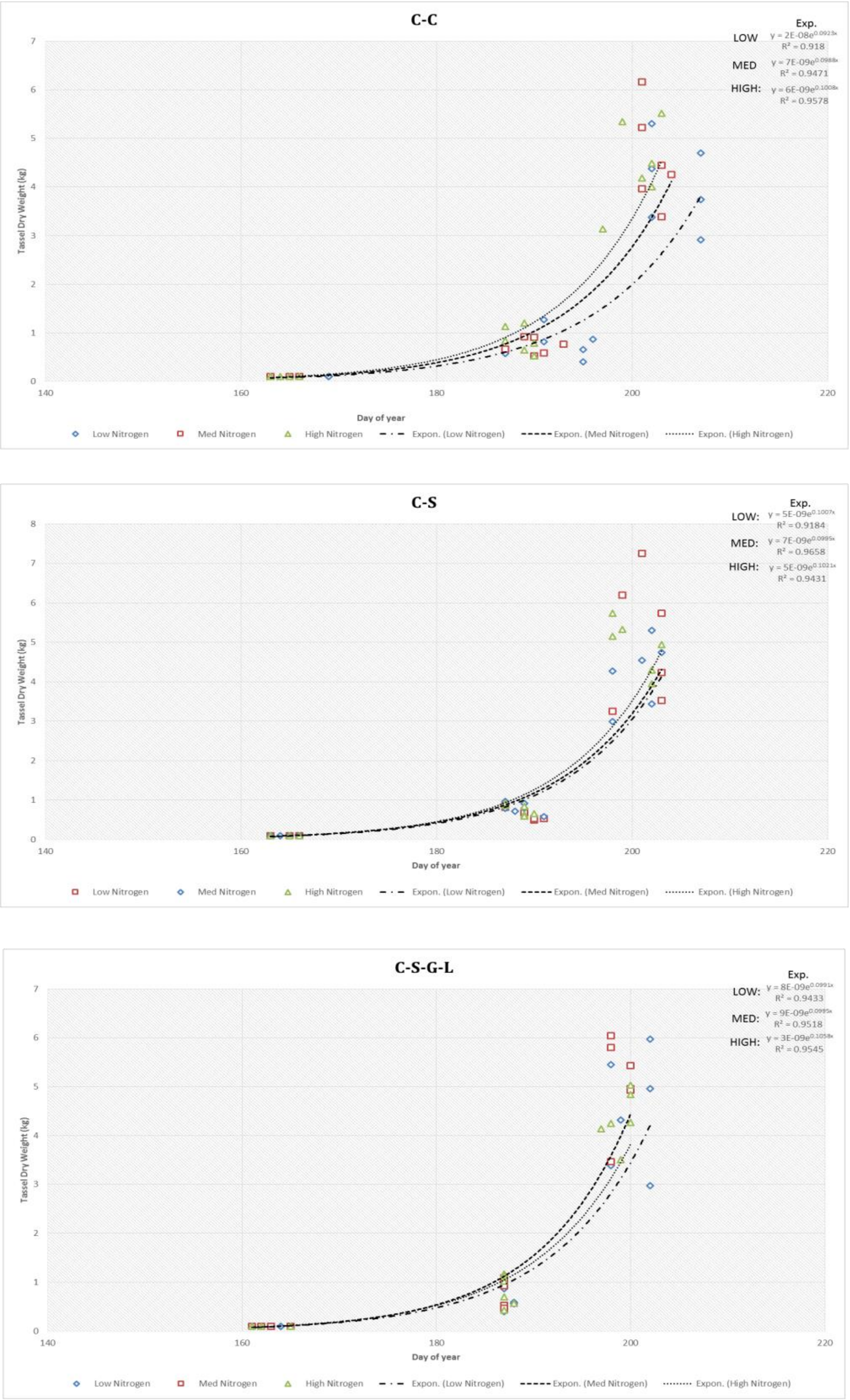

Figure 3.7. Effects of nitrogen application (High, Med, and Low) over time on tassel dry weight for each crop rotation (C-C, C-S, and C-S-G-L)

		Nitrogen : High			Nitrogen : Medium			Nitrogen : Low		
X	Y	CC	CS	CSGL	CC	CS	CSGL	CC	CS	CSGL
sNO3mgkg	sKmgkg	0.228	-0.018	0.500	0.862	-0.126	0.245	0.034	-0.549	0.062
sNO3mgkg	sZnmgkg	0.757	0.016	-0.266	0.270	-0.097	0.156	0.538	-0.495	0.543
sPmgkg	sCamgkg	0.498	-0.281	0.384	-0.701	-0.662	0.248	-0.522	-0.612	-0.076
sPmgkg	sFemgkg	-0.038	-0.131	0.127	0.544	0.858	-0.081	0.353	-0.234	-0.363
sPmgkg	sMnmgkg	0.070	0.026	0.226	0.898	0.701	0.163	0.120	0.354	0.039
sPmgkg	sZnmgkg	0.561	-0.967	0.489	0.549	0.522	0.226	-0.274	-0.646	0.923
sKmgkg	sCamgkg	0.821	0.080	0.045	-0.569	-0.565	-0.838	0.299	0.473	0.597
sKmgkg	sMnmgkg	-0.541	-0.111	-0.519	0.264	0.537	0.889	-0.312	-0.631	-0.161
sKmgkg	sZnmgkg	0.713	0.337	-0.306	0.398	0.639	0.040	-0.779	0.093	-0.376
sCamgkg	sMgmgkg	0.162	0.656	0.829	0.350	0.190	0.287	0.693	0.911	0.786
sCamgkg	sFemgkg	-0.783	-0.772	-0.661	-0.620	-0.486	-0.471	0.191	0.194	-0.269
sCamgkg	sMnmgkg	-0.789	-0.891	-0.663	-0.786	-0.995	-0.699	0.488	-0.492	-0.500
sCamgkg	sZnmgkg	0.255	0.504	0.013	-0.780	-0.121	0.085	-0.162	0.904	-0.107
sMgmgkg	sFemgkg	-0.094	-0.177	-0.697	-0.907	0.736	0.388	0.112	0.270	0.243
sMgmgkg	sMnmgkg	0.027	-0.649	-0.671	-0.782	-0.158	-0.145	0.110	-0.578	-0.151
sMgmgkg	sZnmgkg	-0.425	0.745	-0.249	-0.739	0.642	0.383	-0.806	0.953	-0.604
sFemgkg	sMnmgkg	0.978	0.801	0.956	0.853	0.518	0.731	0.878	0.597	0.810
sFemgkg	sZnmgkg	0.139	-0.051	0.446	0.824	0.633	0.740	-0.111	0.514	-0.396
sMnmgkg	sZnmgkg	0.152	-0.249	0.600	0.801	0.101	0.408	0.112	-0.313	-0.149
pDWg	sNO3mgkg	-0.443	-0.723	-0.322	-0.277	-0.312	-0.871	0.295	-0.367	-0.919
pDWg	sPmgkg	-0.539	-0.143	-0.288	-0.511	-0.169	-0.363	0.752	-0.876	-0.795
pDWg	sCamgkg	0.213	0.830	0.655	0.632	0.590	-0.467	-0.249	0.362	0.326
pDWg	sMgmgkg	-0.326	0.818	0.417	-0.344	0.439	0.112	-0.303	0.557	0.440
pDWg	sMnmgkg	-0.386	-0.939	-0.724	-0.293	-0.550	-0.042	0.384	-0.384	-0.512
pNgkg	sNO3mgkg	0.462	-0.444	-0.268	-0.865	-0.574	0.321	-0.458	0.614	-0.073
pNgkg	sKmgkg	0.410	0.303	-0.336	-0.620	-0.082	-0.615	-0.189	-0.501	-0.929
pNgkg	sCamgkg	0.050	0.875	0.143	0.104	0.841	0.710	0.077	0.136	-0.295
pNgkg	sMgmgkg	-0.958	0.911	-0.170	-0.423	0.389	0.616	0.253	0.444	-0.423
pNgkg	sMnmgkg	-0.094	-0.736	0.513	0.233	-0.831	-0.343	-0.023	-0.209	-0.066
pNgkg	sZnmgkg	0.639	0.774	0.988	-0.110	0.163	0.064	-0.148	0.379	0.497
pPgkg	sPmgkg	-0.600	-0.618	0.389	-0.773	0.009	-0.510	-0.049	0.807	-0.406
pPgkg	sKmgkg	-0.027	-0.154	0.316	-0.242	0.219	-0.509	0.941	-0.019	-0.818
pPgkg	sMgmgkg	-0.264	0.635	-0.236	0.810	-0.644	0.050	0.772	-0.489	-0.326
pPgkg	sMnmgkg	-0.560	-0.294	-0.171	-0.816	0.391	-0.793	-0.469	-0.065	-0.050
pPgkg	sZnmgkg	-0.368	0.687	0.073	-0.578	0.094	-0.731	-0.815	-0.601	-0.094
pKgkg	sNO3mgkg	-0.238	0.142	0.369	0.711	0.344	-0.290	0.229	-0.411	0.036
pKgkg	sKmgkg	-0.768	0.433	0.916	0.383	0.230	0.580	0.944	0.518	0.925
pKgkg	sCamgkg	-0.648	-0.839	-0.296	-0.134	-0.313	-0.673	0.582	-0.168	0.491
pKgkg	sMgmgkg	0.312	-0.345	0.063	0.126	-0.882	-0.731	0.839	-0.360	0.246
pKgkg	sZnmgkg	-0.759	-0.415	-0.198	0.123	-0.438	-0.402	-0.659	-0.424	-0.134
pCAgkg	sNO3mgkg	0.445	0.307	0.741	-0.077	0.399	0.938	0.431	0.938	0.727
pCAgkg	sCamgkg	-0.009	-0.653	-0.073	0.326	0.016	0.141	0.956	-0.549	-0.396
pCAgkg	sMgmgkg	0.155	-0.740	0.200	-0.362	-0.332	-0.159	0.602	-0.278	-0.316
pCAgkg	sMnmgkg	0.184	0.769	0.372	0.247	-0.066	0.413	0.669	0.192	0.671
pMGgkg	sNO3mgkg	0.433	0.160	0.780	0.197	0.522	0.792	0.069	0.638	0.666
pMGgkg	sPmgkg	-0.099	0.737	0.297	0.721	-0.117	0.391	0.361	0.772	0.712
pMGgkg	sCamgkg	-0.662	-0.664	-0.267	-0.270	-0.358	-0.205	0.566	-0.862	0.589
pMGgkg	sMgmgkg	-0.029	-0.837	0.133	-0.298	-0.732	-0.469	0.632	-0.827	0.162
pMGgkg	sFemgkg	0.338	0.426	0.215	0.249	-0.520	0.009	0.725	0.143	-0.398
pMGgkg	sMnmgkg	0.473	0.612	0.404	0.548	0.344	0.529	0.730	0.747	-0.209
pMGgkg	sZnmgkg	0.036	-0.807	0.161	0.215	-0.653	0.232	-0.486	-0.728	0.560
pFEmgkg	sNO3mgkg	-0.412	0.784	0.611	-0.228	0.959	0.082	-0.575	0.321	0.457
pFEmgkg	sCamgkg	0.447	-0.710	-0.293	0.388	-0.232	-0.456	0.141	0.052	0.016
pFEmgkg	sMgmgkg	0.744	-0.761	0.096	-0.433	-0.172	-0.072	0.214	0.047	0.345
pFEmgkg	sMnmgkg	-0.194	0.823	0.072	-0.175	0.282	0.142	0.565	-0.641	0.831
pMNmgkg	sNO3mgkg	0.229	-0.223	-0.329	-0.618	0.158	0.710	-0.193	0.372	-0.260
pMNmgkg	sPmgkg	0.701	0.592	-0.160	0.011	0.378	0.359	-0.301	0.364	-0.257
pMNmgkg	sKmgkg	0.841	-0.818	-0.637	-0.232	-0.469	-0.115	-0.763	-0.128	-0.925
pMNmgkg	sFemgkg	-0.300	0.219	0.939	0.198	0.195	0.219	0.700	-0.021	0.498
pMNmgkg	sMnmgkg	-0.224	0.192	0.852	0.088	-0.255	0.230	0.687	-0.321	0.280
pMNmgkg	sZnmgkg	0.705	-0.520	0.327	-0.187	0.322	0.540	0.355	0.390	0.010
pZNmgkg	sNO3mgkg	0.561	0.326	0.600	0.726	0.171	0.158	0.000	0.563	0.778
pZNmgkg	sPmgkg	0.080	-0.419	0.585	0.177	0.259	-0.078	-0.199	0.628	0.569
pZNmgkg	sKmgkg	-0.242	-0.043	-0.034	0.676	-0.044	0.454	0.765	-0.860	0.005
pZNmgkg	sMgmgkg	0.237	-0.127	0.078	0.468	-0.331	-0.662	0.870	-0.442	-0.021
pZNmgkg	sFemgkg	0.248	0.813	0.149	-0.292	0.027	-0.436	-0.010	0.562	0.152
pZNmgkg	sMnmgkg	0.410	0.752	0.200	-0.002	0.653	0.162	0.127	0.812	0.221
pZNmgkg	sZnmgkg	0.008	0.281	-0.193	0.176	-0.300	-0.780	-0.712	-0.264	0.483
Yieldkgha	sNO3mgkg	0.075	0.244	-0.855	0.586	0.632	-0.635	0.240	0.665	-0.761
Yieldkgha	sPmgkg	0.190	-0.078	-0.440	0.523	0.834	-0.546	-0.738	0.487	-0.648
Yieldkgha	sCamgkg	-0.247	-0.705	-0.021	0.038	-0.500	-0.143	0.713	-0.056	0.211
Yieldkgha	sMgmgkg	0.541	-0.406	-0.376	-0.349	0.303	0.743	0.145	0.174	0.314
Yieldkgha	sMnmgkg	0.116	0.729	-0.283	0.338	0.527	0.061	0.568	0.147	-0.428
Yieldkgha	sZnmgkg	-0.235	-0.060	-0.211	0.189	0.367	0.579	0.354	0.183	-0.339
Oilgkg	sNO3mgkg	0.289	0.250	0.719	0.259	0.539	0.868	-0.471	0.207	0.926
Oilgkg	sPmgkg	0.453	0.613	0.319	-0.757	0.961	0.533	0.234	-0.181	0.676
Oilgkg	sCamgkg	-0.147	-0.874	-0.214	0.348	-0.560	0.608	-0.098	-0.144	0.339
Oilgkg	sMgmgkg	0.286	-0.771	0.169	0.274	0.465	-0.071	-0.002	0.008	0.120
Oilgkg	sFemgkg	0.048	0.398	0.425	-0.328	0.708	-0.289	0.728	-0.767	0.103
Oilgkg	sMnmgkg	0.227	0.622	0.493	-0.602	0.601	0.009	0.416	-0.741	0.353
Oilgkg	sZnmgkg	0.250	-0.777	0.070	-0.016	0.484	0.113	-0.042	-0.253	0.443
Starchgkg	sNO3mgkg	-0.175	-0.681	-0.742	-0.527	-0.740	-0.938	-0.486	-0.634	-0.972
Starchgkg	sPmgkg	-0.360	-0.228	-0.396	0.654	-0.586	-0.574	0.064	-0.280	-0.778
Starchgkg	sCamgkg	-0.059	0.552	0.184	-0.326	0.232	-0.267	-0.704	0.292	0.020
Starchgkg	sMgmgkg	-0.254	0.833	-0.179	-0.454	-0.155	0.479	-0.222	0.080	0.182
Starchgkg	sFemgkg	0.292	-0.268	-0.387	0.538	-0.151	0.417	-0.626	0.728	-0.096
Starchgkg	sMnmgkg	0.110	-0.696	-0.471	0.639	-0.253	-0.161	-0.916	0.618	-0.452
gNgkg	sNO3mgkg	-0.405	-0.115	0.841	-0.366	-0.417	0.819	-0.034	-0.313	0.914
gNgkg	sPmgkg	-0.343	-0.442	0.384	-0.507	-0.310	0.478	0.285	-0.479	0.705
gNgkg	sKmgkg	0.188	0.865	0.138	-0.184	0.639	0.009	-0.655	0.178	0.271
gPgkg	sNO3mgkg	0.072	0.087	0.789	0.219	0.350	0.197	0.848	0.394	0.427
gPgkg	sPmgkg	0.001	-0.309	0.046	-0.774	0.610	0.705	0.168	-0.052	0.843
gPgkg	sMgmgkg	0.021	-0.038	0.089	0.362	0.290	-0.874	0.214	-0.059	-0.386
gPgkg	sFemgkg	-0.449	0.220	0.040	-0.422	0.323	-0.590	-0.105	-0.702	-0.687
gPgkg	sZnmgkg	0.006	0.326	-0.211	-0.148	-0.117	-0.466	0.052	-0.308	0.843
gKgkg	sNO3mgkg	0.626	-0.670	0.403	0.207	0.637	-0.923	0.955	0.559	-0.458
gKgkg	sPmgkg	0.016	-0.175	-0.272	-0.756	0.705	-0.313	0.004	-0.016	0.162
gKgkg	sKmgkg	0.451	-0.463	0.868	-0.106	-0.221	-0.064	0.247	-0.167	-0.245
gKgkg	sFemgkg	-0.091	-0.068	-0.515	-0.336	0.291	0.261	-0.202	-0.451	-0.764
gKgkg	sMnmgkg	-0.027	-0.457	-0.387	-0.616	0.540	-0.231	0.165	-0.501	-0.897
gSgkg	sKmgkg	0.180	-0.768	0.855	-0.307	-0.858	-0.607	-0.717	0.082	0.096
gSgkg	sCamgkg	-0.235	-0.172	-0.254	0.038	0.436	0.602	-0.398	0.597	0.799
gSgkg	sMgmgkg	-0.237	-0.300	0.012	0.182	-0.037	0.739	-0.700	0.633	0.718
gSgkg	sZnmgkg	0.481	0.006	0.114	-0.242	-0.754	-0.071	0.651	0.598	-0.204
gCagkg	sNO3mgkg	0.036	-0.256	0.243	0.495	-0.013	0.310	0.715	0.763	0.111
gCagkg	sKmgkg	0.474	-0.347	0.867	0.121	0.239	0.524	0.611	0.098	0.855
gCagkg	sMgmgkg	-0.392	-0.093	0.304	0.464	-0.377	-0.973	0.220	-0.419	0.675
gCagkg	sFemgkg	-0.567	0.847	-0.854	-0.605	-0.327	-0.352	-0.677	-0.727	0.177
gCagkg	sMnmgkg	-0.512	0.547	-0.754	-0.677	0.079	0.240	-0.329	-0.338	0.178
gMggkg	sNO3mgkg	0.318	0.523	0.844	0.151	0.712	0.920	0.731	0.384	0.755
gMggkg	sPmgkg	0.438	-0.154	0.279	-0.776	0.513	0.785	0.290	-0.041	0.974
gMggkg	sFemgkg	-0.055	0.494	0.165	-0.289	0.044	-0.286	0.429	-0.729	-0.384
gMggkg	sZnmgkg	0.448	0.055	-0.088	-0.050	-0.152	-0.034	0.429	-0.348	0.889
gFemgkg	sNO3mgkg	0.227	0.965	0.503	0.699	-0.296	0.203	-0.230	0.643	0.070
gFemgkg	sPmgkg	0.254	-0.085	0.529	-0.253	0.115	-0.101	0.935	0.746	-0.013
gFemgkg	sKmgkg	0.789	0.099	0.082	0.547	0.066	0.800	0.391	-0.183	0.337
gFemgkg	sCamgkg	0.436	-0.474	-0.092	-0.123	0.584	-0.804	-0.559	-0.041	0.929
gFemgkg	sMgmgkg	-0.437	-0.634	0.037	0.616	0.790	-0.502	-0.051	0.007	0.747
gMnmgkg	sPmgkg	-0.309	0.355	0.911	-0.452	0.841	-0.639	0.138	0.309	-0.760
gMnmgkg	sKmgkg	0.087	0.001	-0.401	0.533	0.500	0.367	0.781	0.075	0.438
gMnmgkg	sCamgkg	-0.358	-0.723	0.234	-0.023	-0.575	-0.467	-0.234	-0.787	0.050
gMnmgkg	sMgmgkg	-0.866	-0.248	0.183	0.660	0.549	0.546	0.325	-0.722	0.510
gMnmgkg	sFemgkg	0.343	0.829	0.260	-0.535	0.930	0.552	-0.671	-0.489	0.482
gMnmgkg	sMnmgkg	0.270	0.571	0.308	-0.509	0.630	0.569	-0.761	0.044	0.398
gMnmgkg	sZnmgkg	0.504	-0.478	0.254	-0.211	0.341	0.187	-0.603	-0.840	-0.934
gZnmgkg	sNO3mgkg	0.554	0.807	0.248	-0.196	0.782	-0.293	0.284	0.889	0.630
gZnmgkg	sPmgkg	0.380	0.346	-0.185	-0.199	0.024	-0.291	-0.068	0.483	0.951
gZnmgkg	sCamgkg	-0.301	-0.345	-0.657	-0.126	0.056	-0.799	0.797	-0.616	0.074
gZnmgkg	sMgmgkg	-0.275	-0.878	-0.357	-0.375	-0.344	-0.432	0.588	-0.305	-0.477
gZnmgkg	sMnmgkg	0.621	0.537	0.555	0.123	-0.049	0.264	0.733	-0.042	-0.087
gZnmgkg	sZnmgkg	0.683	-0.415	0.349	0.469	-0.148	-0.647	-0.172	-0.415	0.828

Figure 3.8. Data Correlation between soil nutrient elements and selected growth parameters

CHAPTER VI:

GENERAL CONCLUSION AND FUTURE WORK

General Conclusion

The use of mathematical and statistical analysis has been shown to be an integral part of the successful development of the bio-renewables industry. The prediction of environmental and economic impacts is an important step in sequestering the potential burdens of unconcerned production bio-renewable based goods. The studies represented in this thesis are examples of the powerful predictions which can be obtained through the TEA and LCA methodologies. The study in Chapter 2 has shown that the conversion of chicken blood to bio-based flocculant, which was empirically hypothesized, is an economically viable operation at commercial scale. Further, select unit operations were highlighted as especially economically impactful, i. e. waste water surcharge and spray dryer fixed costs. Chapter 3 demonstrated environmental and economic incentives for PLA composite production utilizing bio-based filler material (rice husks, wood, and DDGS) and recycling end-of-life treatment. Additionally, use of synthetic filler material (glass and talc) was shown to produce the largest amount of negative impacts over all end-of-life treatments, especially when incineration was applied. Chapter 4 reestablished the conclusions met in the previous parallel study (Riedell et al., 2011). Over the two years' worth of growth data, nitrogen applications were shown to effect growth over all crop rotations. The nitrogen applied during the C-C rotation showed the greatest increase in growth amplitude and speed. During the C-S rotation the nitrogen showed a similar effect as applied to the C-C rotation, but the overall effect was not as significant. Nitrogen applications during the C-S-G-L rotations were shown to have the least effect overall. Further, new interaction trends were observed as well. The soil nutrient elements (N, P, and K) were shown to have various significant interactions with plant dry weight, grain yield, and grain starch content. To conclude, the results documented in these three separate studies were shown to benefit a variety of different areas within the bio-renewable industry, therefore, the results may work well as a precursor for future projects looking to expand or reconfirm the conclusions produced.

Future Work

Looking forward, there are certainly areas where this research may be expanded. Specifically, relative to the research in Chapter 3, there are many future projections which were not considered. If the bio-based flocculant is produced, will the product be applied to purification of human consumed products? If so, the FDA involvement will inevitably have to be considered. Additionally, future market changes, such as the chicken processers potentially beginning to sell their excess blood, will have a direct impact on the results concluded here. Further economic projection modeling of these implications is suggested before any sort of commercialization is considered. The Chapter 4 research leaves room for the inclusion of more detailed equipment and processing options, as well as the need for a more in-depth approach for modeling the pre-processing of raw materials. Many new correlation trends are observed in Chapter 5. It is suggested that future research endeavors empirically investigate the relatively high correlations between soil chemical make-up and important growth characteristics such as yield and starch content. Expanding on the results documented in this thesis may yield potentially beneficial results in these specific areas of the bio-renewable industry.