Optimization and Economics of Small-scale, On-farm Biodiesel Production using Oilseed Crops and Waste Vegetable Oil

by

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Abstract

Recent concerns over unpredictable fuel prices and desire to reduce farm input costs have warranted producer interest in growing alternative crops for the production of biofuels such as biodiesel. Ideally, biodiesel could be produced with a small-scale, on-farm system allowing a farm to retain full value of an oilseed crop. Similarly, on-farm biodiesel feedstock could be supplemented with waste vegetable oil (WVO) from local sources, which would be an inexpensive input to lower production costs. The objectives of this research were to: 1) evaluate the impact of an irrigation regime on oilseed constituents (oil concentration, oil free fatty acid (FFA), and protein concentration) within three oilseed crops (cotton, soybeans, and canola) grown in a non-traditional rotation; 2) determine a biodiesel production and phosphorus removal procedure that could be economical for Alabama farmers and a storage interval for vegetable oil in which FFA will remain within acceptable limits for base catalyzed transesterification; and 3) assess economics of a current small-scale biodiesel production system in Auburn University's Biosystems Engineering department with the data collected being used to develop a prediction model for a small-scale, on-farm biodiesel production system scenario. Five different experiments were performed along with a literature review of biodiesel production practices, efficiency analyses of two mechanical oil extruders, and economic assessments of two small-scale biodiesel production systems. An irrigation experiment examined oilseed constituent responses to varying levels of irrigation for biodiesel production. Triglyceride hydrolysis rates and microbial activity of three vegetable oils were studied over time. The third experiment determined differences in methanol recovery efficiency for two methods. The final two experiments investigated phosphorus removal from

two crude vegetable oils, quality of biodiesel produced, and phosphorus removed resulting from transesterification.

Results from the irrigation experiment indicated that seed and oil yields significantly improved with irrigation and rainfall. As a result, theoretical biodiesel yields increased 380%, 166%, and 200% for soybean, cottonseed, and canola, respectively. Protein concentrations tended to decrease with irrigation, but FFA values showed little response with emphasis on biodiesel production except when seeds were exposed to excessive end of the season moisture. Based catalyzed transesterification with methanol and sodium was determined to be least expensive yielding favorable results. WVO and canola oil oxidized 68% and 43% during storage and no microorganism activity was detected. While soybean oil oxidized 50%, FFA levels remained well under one percent. Vacuum pump assistance increased methanol recovery by 600%. ASTM requirements of phosphorus removal were not met during oil degumming experiments. Bench scale transesterification reactions resulted in higher ester conversion than the Biodiesel Logic, Inc. processor due to increased oil/methanol interaction, but AMBERLITE™ BD10DRY satisfactorily removed free glycerin from biodiesel. A mechanical screw press with fixed components required less operator aptitude to increase oil extraction of canola, however soybean oil extraction proved efficient on the Henan Double Elephant mechanical press. Oil extraction efficiency was heavily dependent on oilseed moisture content and operator ability. WVO biodiesel cost of production was $0.58/L while soybean and canola biodiesel production costs were substantially higher. However in 2010, Alabama soybean farmers could have reduced losses by $24.70/ha when producing biodiesel as opposed to selling crops through traditional market outlets.

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Table of Contents

List of Tables

List of Figures

CHAPTER ONE
INTRODUCTION

1.1 **Problem Statement**

Emphasis on alternative energy in the U.S. has increased with the desire for fuel independence and threat of petroleum oil scarcity. One heavily researched outlet for bioenergy production is biodiesel. Biodiesel can be produced from any renewable fat or oil source (e.g. animal fat or vegetable oil) and requires little to no infrastructure or diesel engine modifications to transport and store or utilize, respectively. In recent years, various large scale production plants were established around the country to produce biodiesel, but many have since ceased production. "Growing pains" in large scale biodiesel production (Crooks, 2008), are the result of increasing commodity prices and logistics of transportation costs. But commodity prices have not suffered alone as a result of market volatility. Many farming inputs (e.g. fertilizer and fuel) have become unstable in recent years, leaving some profit margins in the red. Figure 1.1 illustrates market price fluctuation in soybeans and diesel fuel over the past 30 years (USDA NASS) demonstrating recent increase. Given this data, it is understandable how in 2009 Alabama soybean farmers experienced an average profit of $53/ha, but a loss of $250/ha in 2010 (ACES, 2011). A requisite for consistent and manageable farming input costs is imperative for the future of sustainable agriculture.

Implementation of a small-scale, on-farm biodiesel production system could provide normalcy and security in the midst of volatile markets by giving farmers more options for maximizing returns on their crops and minimizing potential losses as experienced several times in recent years. Biodiesel could

be produced from portions of oilseed crops grown on farm, supplementing yearly fuel and livestock feed requirements, or crops could be sold through traditional commodity markets. This scenario allows the farmer to weigh his options each year and determine where the most economic gain can be achieved. Despite the recent increase in commodity markets, Faircloth (2008) suggested that if farmers could

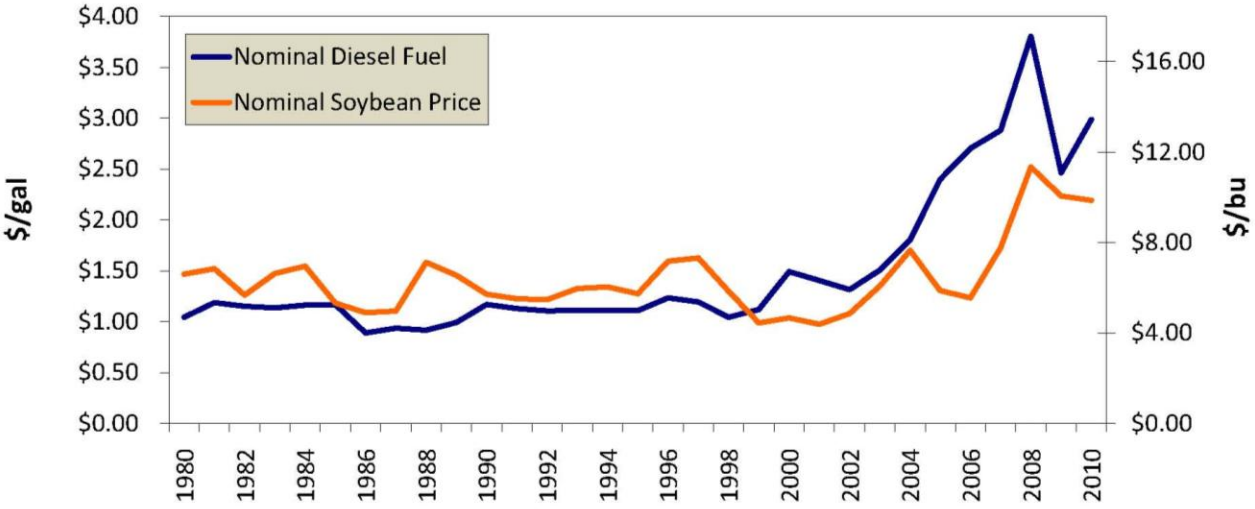

Figure 1.1. Soybean and diesel fuel prices from 1980 – 2010 (USDA NASS, 2011).

develop on-farm processing and handling of oilseeds, the value of (vegetable) oils would be retained on the farm and producers might have an opportunity to become more fuel independent, thus relinquishing total reliance on one unpredictable parameter, the petroleum fuel market. However, in terms of farming operations in which bioenergy crops may be grown to facilitate on-farm fuel demand and in the event small-scale, on-farm biodiesel production facilities are employed, limited research exists on the effectiveness of pragmatic development and operational aspects of an integrated system. Research highlighting methods of managing on-farm biodiesel production cost and bringing a system such as this to fruition in current markets are also limited. Therefore, the scope of this research covered oilseed crop constituent responses to irrigation that were important for biodiesel production, practical methods of processing crude vegetable oils in preparation for transesterification and techniques to increase biodiesel processor efficiencies and end product quality. Economic assessment of a current

small-scale biodiesel production process was ascertained and the data acquired was used to predict production costs for an on-farm scenario and assist in determining how to minimize production costs. This research will allow the feasibility and economic impacts of a small-scale, on-farm biodiesel production system to be better understood in order to equip Alabama farmers with vital decision making tools and opportunities that will ensure successful future farming operations.

1.2 **Research Objectives**

The main goal of this experiment was to investigate practical parameters of small-scale, on-farm biodiesel production that would increase the efficiencies and effectiveness of oilseed production and oil and biodiesel processing techniques; ultimately resulting in quality end products that would benefit Alabama farmers. Therefore, the objectives of this research were to:

1. Evaluate the impact of an irrigation regime on oilseed constituents (oil concentration, oil free fatty acid (FFA), and protein concentration) within three oilseed crops (cotton, soybeans, and canola) grown in a non-traditional rotation,
2. Determine a biodiesel production and phosphorus removal procedure that is economical for Alabama farmers and a storage interval for vegetable oil in which FFA will remain within acceptable limits for base catalyzed transesterification, and
3. Assess economics of a current small scale biodiesel production system in Auburn University's Biosystems Engineering department with the data collected being used to develop a prediction model for a small-scale, on-farm biodiesel production system scenario.

1.3 **Thesis Organization**

The *Introduction* chapter provides a brief overview of problems currently facing biodiesel production systems along with the goals of this research. The *Literature Review* highlights previous

research on topics related to the objectives of this project and additional pertinent material. Next, chapter three *Research Methods* outlines equipment, procedures, design and data that will be collected for each experiment. The *Results and Discussion* chapter reports collected data and analysis along with discussion to support the results. Finally, the last chapter offers experimental summary and final conclusions for this study along with suggestions for future research.

CHAPTER TWO
REVIEW OF LITERATURE

2.1 Introduction

In today's economy, alternative energy production is a popular topic of discussion in arenas of academia, industry and small businesses such as family-owned farms. Knowledge dissemination, especially for biodiesel production, is allowing the average person to begin trying his hand at shade-tree, small-scale biodiesel manufacturing in hopes of alleviating partial dependence on petroleum fuels. However, questions still remain as to best practice methodologies of optimizing feedstock production and processing techniques and practical means of obtaining a quality end product and economics of a small-scale biodiesel production system. To begin studying the topic of optimization and economics of small-scale, on-farm biodiesel production using oilseed crops and waste vegetable oil, previously performed research has been carefully reviewed. This chapter presents previous research and experimentation on various issues including crop responses to irrigation, oil refining, oil and biodiesel stability, biodiesel production, and economics.

2.2 Oilseed Response to Varying Irrigation

In the southeastern United States where rainfall can be limited during the growing season, irrigation is utilized to minimize crop yield variability from year-to-year, maximize yield and increase return. New technology such as variable-rate irrigation could improve in-field water use efficiency. Additionally, with the rise in fuel prices, producers have become interested in growing alternative crops for the production of biofuels such as biodiesel. An ideal oilseed used for biodiesel production would

include high oil and protein concentrations along with low oil free fatty acid (FFA) constituents. With a high level of protein, the co-product or cake, from the mechanical oil extraction process could be used as a protein increasing livestock feed ration supplement. Likewise, a high concentration of oil would lend itself to increased yields of biodiesel and a low concentration of FFA would allow for simple transesterification techniques to be used. According to Livingston et al. (1995), Faircloth (2008) and Boydak et al. (2002), canola contains about 40% oil while cottonseed and soybeans range from 18% to 25% oil. However, these oilseed constituents may be affected by irrigation at different levels.

Cottonseed, soybeans, and canola have seed properties favorable for our intentions as well as climatic growing requirements experienced in the southeastern United States and irrigation at a certain level may facilitate these properties rendering them more favorable for biodiesel production. Traditionally, cotton has been the predominant crop grown in the southeastern United States and, according to Sawan et al. (2006), cottonseed meal is classed as a protein supplement in the feed trade. However, soybean is the primary oilseed used in U.S. biodiesel production at present (Faircloth, 2008). The actual composition of soybeans depends on many factors, including genotype, growing season, geographic location, and agronomic practices (Boydak et al., 2002). This statement holds true for not only soybeans, but also a majority of agronomic crops including canola and cotton.

2.2.1 Oil Concentration

With soybean being the dominant oilseed crop in the US and maintaining substantial presence in commodity markets alongside its derivatives of oil and meal, understanding irrigation and soybean oil concentration interaction is especially important. Bellaloui and Mengistu (2008) experimented with two cultivars of soybeans (*Dwight* and *Freedom*) and three irrigation regimes (full-season irrigation; FS, reproductive stage/supplemental irrigation; RI, and non-irrigation; NI) to compare yield and seed composition differences. This experiment was conducted at the Delta Research and Extension Center, Stoneville, MS. They found that *Freedom* resulted in higher oil percentages under FS and RI than *Dwight*

but 2004 was the only cropping season in which significant differences were experienced with a mean difference of 1.3%. However, under NI conditions, *Dwight* resulted in higher oil accumulation (23.5%) compared to *Freedom* (17.8%). There work suggested that seed composition differences may be attributed to cultivar, maturity group, water stress and/or adaptability to irrigation.

Boydak et al. (2002) experimented with irrigation and row spacing on oil concentration in soybeans in the Harran region of Turkey. Irrigation was performed every 3rd, 6th, 9th, or 12th day. They found that oil concentration was not significantly different for soybeans irrigated on the 3rd, 9th or 12th day and 6th day irrigation intervals resulted in lowest oil yield. It is unclear as to the degree of significance because the oil concentration P value for 6th day irrigated soybean was not reported, but the mean oil concentration was only one percent lower than the average of high oil yielding treatments. And in a similar study, Ibrahim and Kandil (2007) explained yield and chemical constituent effects of soybeans due to irrigation and plant row spacing in Egypt. Soybeans were irrigated at 7, 14, and 21 day intervals. No significant differences were observed during the two years of the study for oil concentration responses to irrigation with averages ranging from 19% to 20%. The work of these researchers recognized that irrigation was an important factor in facilitating crop yield, but irrigation intervals from 3 days to 21 days did not impact oil production in soybeans.

Sprecht et al. (2001) measured oil concentration response to water replenishment of soybeans. Plots were irrigated at varying levels of 0%, 20%, 40%, 60%, 80%, and 100% pan evaporation replenishment. During the 1995 growing season, drought allowed the full water potential to be measured with 100% pan evaporation replenishment plots requiring 41-cm water. They found that increasing irrigation decreased oil concentrations from 18.1% to 17.5% for 0% to 100% pan evaporation replenishment, respectively. This result suggested that increased water quantity, not irrigation interval, may negatively impact oil concentration in soybeans.

Canola, being genetically developed in and native to Canada is traditionally a spring crop. However, in the southeast US, it is grown as a winter crop as this season's climatic conditions more closely follow those of springtime in Canada. According to Livingston et al. (1995) and Neilsen (1998), canola may contain a range of 36.6% to 44.2% oil concentration. Similar to findings of Sprecht et al. (2001) for soybeans, Sims et al. (1993) found that increased water led to decreased oil content in canola. Taylor et al. (1991) found that no irrigation of canola coupled with increasing nitrogen rates, from 0 kg/ha to 200kg/ha, decreased oil content from 46.4% to 40.6%, respectively. However, irrigated plots experienced increased oil but a similar trend existed in which nitrogen rate increase caused a decrease in oil content. This leads to a conclusion that irrigation alone may not necessarily be the deciding factor in oil concentration within a canola seed. Other parameters such as macronutrients, in this case nitrogen, may have an impact on oil concentration within canola seeds.

2.2.2 Protein Concentration

On average, 35% to 45% protein can be expected in soybeans (Boydak et al., 2002). However, protein content may be influenced by irrigation according to Ibrahim and Kandil (2007) who found that increased irrigation intervals for soybeans resulted in increased protein concentrations. On the other hand, severe drought led to decrease in protein concentration in soybeans (Specht et al., 2001).

In the study by Bellaloui and Mengistu (2008) outlined above, *Dwight* exhibited higher protein concentrations under FS and RI than NI, however, Freedom resulted in higher protein percentages under NI. Freedom exhibited the highest level of protein for both cultivars during the experiment under NI (45.5%). As with oil concentration, cultivar differences appear to impact protein concentration as *Dwight* responded positively to irrigation but *Freedom* responded positively to non-irrigation.

In addition to measuring oil concentration responses of soybeans to varying levels of irrigation as illustrated above, Sprecht et al. (2001) measured protein concentration responses as well. They found that by increasing irrigation, protein concentrations increased from 44.8% to 46.0% for 0% to 100% pan

evaporation replenishment, respectively. Soybean experiments by Chung et al. (2003) closely followed those of Sprecht et al. (1986, 2001) with an explicit negative correlation being made between oil content and protein. To quantify this assessment, Chung et al. (2003) irrigated a hybrid soybean with one of six irrigation regimens: 0%, 20%, 40%, 60%, 80%, and 100% replacement of weekly evapotranspiration. They found that protein concentration was enhanced with incremental seasonal irrigation increases, while oil content was decreased.

Boydak et al. (2002) and Ibrahim and Kandil (2007) took a slightly different approach by experimenting with interactions between irrigation and row spacing on protein concentration in soybeans with experimental procedures being conducted as outlined above. Boydak et al. (2002) found that protein concentrations were not significantly different for 3rd, 6th, and 9th day irrigated beans with 3rd day irrigated beans exhibiting highest protein yields (38.6%) and 12th day lowest (37.6%). This research parallels the findings of Bellaloui and Mengistu (2008) with certain cultivars but contrasted Ibrahim and Kandil (2007). An intermediate interval of 14 days resulted in highest protein concentration of 28.9% as opposed to 7 day or 21 day irrigation intervals (Ibrahim and Kandil, (2007). Along with diverging experimental results, overall protein percentages were different as well. Suggestions of Boydak et al. (2002) may once again explain this discrepancy by recognizing that genotype, growing season, geographic location, and agronomic practices can significantly impact oilseed constituents.

2.2.3 FFA Concentration

Free fatty acid (FFA) concentration is among the most important constituent of oilseeds for biodiesel production. Along with high yields of oil, irrigation effects on FFA concentrations are of importance for biodiesel production since it has been reported that high levels of FFA in canola oil, in particular, hasten rancidity (hydrolysis) and shorten the shelf life of the oil. Levels of FFA above 1% result in extra costs for removing the FFA from the oil (May et al., 1994). Low concentrations of FFA in

vegetable oil are desirable for the aforementioned reasons and because it will minimize the amount of catalyst required for the biodiesel process and avoid the potential for acid catalysis pretreatment.

In the experiment of Boydak et al. (2002) outlined above, FFA values were measured in addition to oil and protein concentrations. They reported that FFA concentrations are dictated by variety, planting date, and meteorological factors. Oleic acid content was found to be highest for 12^{th} day irrigation of soybeans as opposed to 3^{rd}, 6^{th}, or 9^{th} day irrigation intervals and correlated to oil concentration increase as well.

Lee et al. (2008) investigated unsaturated fatty acid content in soybeans in modified varieties under irrigation and rainfed scenarios in Missouri. They found that irrigation had no significant effect on unsaturated fatty acid accumulation in soybeans but significant differences did exist over years. However, trends existed in eight of the nine varieties studied, in which oleic acid (18:1) was higher in irrigated plots than non-irrigated plots. They suggested that fatty acid levels correlate to growing season temperature. Two- and three-way interactions of year, environment and genotype, excluding irrigation, resulted in significant differences for fatty acids.

In the two cultivars of soybeans studied by Bellaloui and Mengistu (2008), *Dwight* and *Freedom*, FFA concentrations were not consistent in their response to irrigation but cultivar differences were observed averaging 30% more FFA in *Dwight* as opposed to *Freedom* for the three irrigation treatments. Their results correspond to the research above suggesting that factors other than irrigation can have a profound impact on FFA and fatty acids in oilseeds.

To investigate factors that may lead to FFA accumulation in oilseeds, Evans et al. (1974) capitalized on an anomally that illustrated the potential of factors outlined by Boydak et al. (2002). Harvest and crude oil quality of the 1974 southeastern U.S. soybean crop was poor as measured by FFA accumulation. Damage to soybeans is known to increase FFA in crude oil. FFA increase was believed to be a direct result of prolonged moisture exposure in the field experienced in November of 1974.

Extensive field and storage damage to soybeans was reported to be 25% to 35%. Once the bean was ready for harvest but was exposed to excessive moisture, the lipase enzyme is activated (Smouse, 1995) within the soybean and germination is initiated. In order for the seed to reach emergence, energy was needed. This energy was obtained from the breakdown of triglycerides, thus releasing FFA and creating diglycerides and eventually monoglycerides. This reaction and energy release supports the early stage of the soybean plant until the root system is established to acquire energy through nutrient and water uptake and begin photosynthesis. Smouse (1995) went on to suggest that prolonged moisture exposure and/or split beans will contain higher non-hydratable phospholipids with split beans containing higher FFA levels. If seeds have been damaged by heat, wet weather, excessive moisture, poor storage, or other damaging conditions, then the crude oil obtained will require further processing to obtain an edible or usable product plus have poor stability during storage.

May et al. (1994) investigated the effects of agronomic practices on spring canola FFA levels in Ontario, Canada. Canola plots were irrigated every fourth day with 2 cm of water until physiological maturity. They suggested that decreasing seeding rates, high nitrogen, delay in planting date, and drought stress will raise FFA levels in canola. However, irrigation during seed filling decreased FFA levels. Irrigation increased yield and oil content but decreased FFA during this study, although the effects of irrigation on FFA were not significant within years. Increasing seeding rates from 1 to 9 kg/ha resulted in lower FFA, 0.54% to 0.35%, respectively. Likewise, 200 kg/ha nitrogen application resulted in the highest yield, lower oil yield and highest FFA concentrations as opposed to the 100 kg/ha and 0 kg/ha nitrogen rate treatments.

Taylor et al. (1991) found that rainfed conditions increased FFA in canola but Boydak et al. (2002) reported that irrigation had no significant effect on FFA levels in canola. Data from these researchers coupled with the research above, further solidifies the statement by Boydak et al. (2002)

that irrigation may have an effect on oilseed constituents, but interactions among environmental factors, agronomic practices and cultivars account for much of the significant differences experienced.

2.2.4 Yield

It has long been an accepted theory in the scientific community that irrigation facilitates crop yield. Nevertheless, no one parameter can be singled out as the determining factor in crop performance or yield. In the study by Bellaloui and Mengistu (2008), irrigation, cultivar and year were found to be highly significant ($P \leq 0.01$) for yield differences. Irrigation proved to increase yield in both cultivars (approximately 100% and 30% increase in two of the three years of the study for *Dwight* and *Freedom*, respectively), however yield was also dictated by cultivar and growing conditions (such as soil water content and temperature) for the respective years.

Sprecht et al. (2001) measured water response of soybeans on yield concentration. Plots were irrigated with 0%, 20%, 40%, 60%, 80%, and 100% pan evaporation replenishment. During the 1995 growing season drought allowed the full water potential to be measured with 100% pan evaporation replenishment plots requiring 41 cm water. They found that increasing irrigation increased yield from 933 kg/ha to 2,085 kg/ha for 0% to 100% pan evaporation replenishment, respectively.

Similarly, Chung et al. (2003) experimented with the same irrigation treatments applied to replace weekly evapotranspiration. They discovered correlations among yield, protein concentration and oil concentration such that yield and protein were enhanced with incremental seasonal irrigation increases, while oil content was decreased. These finding correlated to Sprecht et al. (1986, 2001). However, Ibrahim and Kandil (2007) found that an intermediate, 14 day irrigation interval had the most impact on yield rather than row spacing. Fourteen day irrigation intervals resulted in highest yield compared to 7 day and 21 day intervals and the interaction between irrigation interval and row spacing resulted in 14 day irrigation coupled with 10-cm, 20-cm and 30-cm row spacing yielded highest soybean harvest of all treatment interactions, respectively.

It has been reported that the highest yields of canola will be obtained when adequate soil moisture is maintained throughout the growing season (Thomas et al., 1986) suggesting that sufficient rainfall or higher levels of irrigation are required to optimize yield in canola. Imtiyaz et al. (2000) researched yield under variable irrigation, 20%, 40%, 60%, 80%, and 100% pan evaporation replenishment. They found that the highest marketable yields of rape at 80% pan evaporation replenishment through irrigation. This level is speculated to have provided adequate soil moisture as recommended by Thomas et al. (1986). Irrigation production efficiency was highest at 20% pan evaporation replenishment; however, yields did increase with irrigation replenishment but did not result in profitable yields considering the seasonal application of water required at higher irrigation levels.

Likewise, Sims et al. (1993) found that increased irrigation led to increased yield. In Alberta, Canada, canola produced seed yields of about 1000 kg/ha with 20 cm of water. Each additional 2.54 cm of water resulted in 150 kg/ha increase in yield, Anonymous (1985). Likewise, Nutall et al. (1992) found that canola yield in Saskatchewan, Canada increased by 150 kg/ha for each additional 2.54 cm of precipitation in July and August. However, Rife and Salgado (1996) stated the winter-type canola varieties generally have greater yield potential than spring-type varieties.

In addition to irrigation and as is the case in other agronomic crops, irrigation alone is not be the sole driving force behind crop yields. Taylor et al. (1991) investigated yield responses of canola to irrigation and nitrogen application. Plots were rainfed or irrigated at 50-mm deficit with 0, 50, 100, or 200 kg N/ha applied. They found that increased nitrogen and irrigation levels on canola increased yield. They recommended that a minimum nitrogen rate of 100 kg/ha was required to optimize canola yield. Any additional nitrogen would increase yield but may induce lodging because of excessive vegetative growth and plant height, ultimately resulting in yield loss.

Because cotton is typically valued for its lint yield, research is limited on cottonseed responses to irrigation, environmental factors, agronomic practices, etc. As reported by McKevith (2005)

cottonseed averages 32.6% protein making it a valuable protein increasing livestock feed supplement which is already the case for most of cottonseed in the US at present. However, it appears that macro and micronutrients can influence cottonseed and cottonseed constituents. Sawan et al. (2006) found that cottonseed oil content, protein content and yield could be increased and oil FFA could be decreased with applications of potassium, zinc, and phosphorus. However, FFA differences were not significant at 95% confidence interval.

2.3 Oil Degumming

Vegetable oil degumming is standard for commercial and industrial practices. Gums can cause problems during the transportation of oils by settling and forming deposits on tank walls or clogging pipelines. In engines where vegetable oil or biodiesel is used, gums or phospholipids can cause catalytic converter issues or coking within the engine. Mittelbach (1996) reported that increased phosphorus content in biodiesel can result in higher particulate emissions, possibly influencing the effectiveness of the catalytic converter. He also suggested that fully refined oils, in theory, should have less phosphorus concentrations than non-refined oils and that transesterification can lower phosphorus levels from over 100 ppm down to 20 – 30 ppm. Cvengros and Povazanec (1996) stated that cold pressing is ideal for a farm level biodiesel operation. There is little phospholipid output and the protein in the cake is not denatured, providing a good livestock feed ration supplementation.

Brekke (1980) summarized several techniques of vegetable oil degumming frequently used by practitioners. He stated that there are two types of phosphatides in vegetable oils, hydratable and non-hydratable. Hot water can be used to remove hydratable phosphatides from oils. Once mixed with water these hydratable phosphatides swell to form gels of higher density than oil. They will tend to gravitationally separate from the oil and can be removed. However, for best separation of the oil and gum layers, centrifugation should be used. Non-hydratable phospholipids may be removed through the

use of reagents such as citric acid, phosphoric acid, and hydrochloric acid, among others. When using water to degum vegetable oils, the proper amount was recommended at 75% of the oil's phosphatide content.

Choukri et al. (2001) experimented with a modified procedure for soft degumming of soybean oil. Two wt.% hot water was used to remove hydratable phospholipids from the soybean oil, then a 5% aqueous solution of chelating agent (EDTA) and emulsifying agent (sodium dodecyl sulfate, SDS) was added. Phosphorus concentration was assessed according to AOCS method Ca 12-55 (2009j). They found that dephospholipidation was directly related to the increased concentrations of EDTA or emulsifying agent. Differences observed for varying phosphorus concentrated oils were attributed to cation content. Higher cation content is thought to decrease the chelating agent's effects on phosphorus removal. Concentrations of EDTA and emulsifying agent higher than 50 mM and 30 mM, respectively removed adequate amounts of phosphorus in oils containing 46 ppm initial phosphorus so that it adhered to ASTM standard D6751 (2007) in terms of phosphorus concentration (10 ppm). The research did not yield favorable results for oils initially containing >180 ppm phosphorus. When a hot water method of phospholipid removal was used to remove hydratable phospholipids first followed by EDTA and an emulsifying agent, a 10% aqueous solution of 50 mM emulsifying additive removed sufficient amounts of phosphorus so that the oil adhered to ASTM D6751 (2007) standard of 10 ppm maximum phosphorus. Temperatures greater than 65 ^{o}C resulted in best results of phosphorus removal and were attributed to the phospholipid structure. Incubation time results were best at 20 minutes. Longer times resulted in increased phospholipid concentrations due to scattering of phospholipidic esters as fine particles in the oil phase and thereby reducing centrifugation efficiency. Using a minimum of 150 mM of EDTA and 50 mM of emulsifying agent, in conjunction with hot water degumming, resulted in less than 5 ppm phosphorus for tested oils (linseed, soybean, colza, sunflower, and palm); the efficiency was independent of initial phosphorus concentration.

Cvengros et al. (1999) used degummed canola oil as an alternative diesel engine fuel. They stated that canola oil containing less than 20 ppm phosphorus can be obtained by simple cold pressing of oilseeds. They obtained mechanically pressed oil and used a hot water procedure of 0.8 wt% water to remove phosphorus. The oil was heated to 80 ^{o}C then the water was added and gently stirred for 20 minutes. In their experiment, cold pressed canola oil contained 14.6 ppm phosphorus while coldpressed/extracted oil contained 352 ppm phosphorus. After degumming, phosphorus concentrations were 13.4 ppm and 216 ppm, respectively. Bleaching the canola oil with bleaching clay resulted in further phosphorus removal down to 5.4 ppm and 186 ppm, respectively. Of particular interest, Cvengros et al. (1999) found that a considerable amount of phosphorus goes into the glycerol phase of transesterification. Unrefined canola oil containing 14.57 ppm phosphorus, initially, exhibited only 3 ppm phosphorus after transesterification. Likewise, refined oil (5.23 ppm phosphorus, initially) contained only 0.23 ppm phosphorus after transesterification. If biodiesel feedstock is obtained through mechanical pressing, phosphorus concentrations should be relatively low without a degumming procedure. However, this level is not as low with pressed/solvent extracted oils. Phosphorus concentrations are significantly higher and require intensive refinement to meet ASTM standard D6751 (2007) for phosphorus concentrations. Once transesterification of the cold pressed vegetable oils is conducted, phosphorus concentrations should be well within ASTM D 6751 (2007) limitations, 10 ppm.

Phospholipids are one parameter attributed to yield losses during transesterification of vegetable oils. Du et al. (2004) experimented with transesterification of crude and refined soybean oils. Yield losses in biodiesel from crude oil vs. refined oil were attributed to phospholipid concentrations, FFA, and water content. Phospholipid content was found to be the most limiting factor in that as phospholipid concentration increased, biodiesel yield decreased. While a lipase enzyme (Novozym 435) was used for transesterification, Du et al. (2004) found that ester yield was substantially lower for crude oil vs. refined oils. Although phosphorus may be removed during transesterification as stated by

Cvengros et al. (1999), there is potential for ester yield losses if not removed before transesterification takes place.

Evans et al. (1974) analyzed phosphorus concentrations in damaged soybeans from the Southeast, Midwest, and Southwest U.S. Contrary to Brekke (1980), they found that crude oil from damaged beans, on average, contained low levels of phosphorus, less than 500 ppm. While Brekke (1980) and Smouse (1995) suggested that damage beans will have higher phosphorus content, in particular non-hydratable phospholipids. However, the oil from these beans was solvent extracted which Brekke (1980) suggested causes exhibition of high levels of phosphorus as opposed to mechanically extracted soybean oil. Given that damaged beans contain less phosphorus than normal beans and mechanical extraction releases less phosphorus than solvent extraction, it stands to reason that damaged beans, having little value as a food-grade product may hold potential as a biodiesel feedstock. But for this scenario to reach fruition, the oil must be mechanically extracted. Oil mechanically extracted from damaged beans should exhibit lower phosphorus content as opposed to solvent extracted oil from normal soybeans.

Many researchers report satisfactory results of acid degummed oils. List et al. (1978) is not different as they researched the effects of phosphoric acid and water degumming on phosphorus removal. They discovered that phosphoric acid pretreatment before water degumming resulted in similar phosphorus levels as water degumming alone. With water, phosphorus levels could be lowered from 660 ppm to 53 ppm. With a further water wash and bleaching, phosphorus levels could be further lowered to 15 ppm. Using phosphoric acid pretreatment with water degumming and water washing and bleaching resulted in 3 ppm phosphorus. List et al. (1978) also made an observation that optimal oxidative stability of oil was obtained with phosphorus levels ranging from 2 ppm to 20 ppm.

McDonnell et al. (2000) were concerned with high cost feedstocks of rapeseed methyl esters in Europe and experimented with adding rapeseed oil to conventional diesel fuel as a diesel fuel extender.

The rapeseed oil was degummed using acidified hot water and filtration down to 5 microns. Adverse results were reported in terms of shorter service intervals when operating equipment with 15% semi-refined rapeseed oil using their method. However, in direct injected diesel engines, common to most agricultural tractors, this diesel fuel extender provides potential.

Smiles et al. (1988) experimented with six reagents to degum canola, soybean and sunflower oils. They determined that citric acid or phosphoric acid, in conjunction with water, were effective at removing 91% and 93% phosphorus, respectively. For soybean oils, all reagents except solely water performed satisfactorily in removing up to 98% of the phosphorus. The initial phosphorus concentration of canola oil samples was 617 ppm. Water, citric acid, and phosphoric acid lowered phosphorus levels in canola oil to 247 ppm, 57 ppm, and 45 ppm, respectively. Soybean oil initially contained 716 ppm phosphorus while water, citric acid, and phosphoric acid were effective in reducing phosphorus levels to 100 ppm, 14 ppm, and 15 ppm, respectively.

Many reagents have been experimented with as potential degumming tools. Diosady et al. (1982) experimented with 54 reagents on canola oil. The oils degummed were samples that had been expelled or mechanically pressed, and extracted or solvent extracted. Similar to findings of Cvengros et al. (1999), Diosady et al. (1982) found that mechanically pressed oils exhibited less than 30% phosphorus to that of solvent extracted oils. Degumming procedures were performed exactly the same for all 54 reagents with results showing phosphorus level reduction from 508 ppm to 167 ppm, 102 ppm, 35 ppm, for water, phosphoric acid and citric acid, respectively. The most effective reagent in terms of phosphorus removal was hydrochloric acid resulting in 23 ppm. Diosady et al. (1984) took their results from previous research and extrapolated them to a pilot scale plant. They researched optimizing oil degumming with citric acid. Oil contact times with the reagent and water were each optimized at 30 minutes, resulting in 38.2 ppm phosphorus concentrations in a pilot scale degumming process. Results were similar to ones obtained through laboratory scale experiments.

Zufarov et al. (2009) experimented with degumming rapeseed and sunflower oils with water, acid, and other methods. They found that water degumming reduced phospholipids concentrations from 445 ppm to 51.1 ppm in rapeseed oil and from 163 ppm to 44.2 ppm in sunflower oil. They concluded that water degumming alone is insufficient in adequate removal of phospholipids. Citric acid was also used for phosphorus removal. Zufarov et al. (2009) stated that citric acid will convert non-hydratable phospholipids to hydratable phospholipids while working as a chelating agent to keep metals in a water soluble complex. This method reduced phosphorus from 445 ppm to 8.7 ppm in rapeseed oil and from 163 ppm in sunflower oil to 5.2 ppm.

Like soft degumming, a dry degumming method can potentially prove effective at removing phospholipids from vegetable oils. Koris and Vatai (2002) experimented with dry degumming of soybean oil through membrane filtration. The molecular weight of triglycerides and phospholipids are 900 g/mol and 800 g/mol respectively. Phospholipid molecular size is between the range of ultra-filtration (UF) and nano-filtration (NF) so a UF/NF membrane was used in the experiment. They found that 70% to 77% phospholipids could be retained on the membrane filter by heating the oil to 40-60 ^{o}C pressurizing the system to 2-5 bar and having an oil flow of 0.3-0.4 L/m^3 in the system. This retention percentage was only obtained after adding 5% water to the oil when using a membrane of 0.2 μm pore size. Apparently, the hydratable phospholipids swelled and were able to be retained because of larger particle size. ASTM standard D6751 (2007) was not met with membrane filtration of soybean oil in this experiment as all membrane filtration tests resulted in greater than 10 ppm phosphorus concentrations.

2.3.1 Issues with the Degumming Process

Smouse (1995) suggested that if oils are kept at high temperatures, phospholipids will not be easily removed. Cooling crude oil results in easier water degumming properties but prolonged storage inhibits degumming effectiveness. The more crude oil is cooled, the longer it can be stored and still

possess excellent water-degumming properties. However, phospholipids have shown to be effective antioxidants and chelation agents and will increase the oxidative stability.

2.3.2 Preparing Seeds for Extrusion

Some methods of mechanically pressing oilseeds to extract oil suggest that the seed be heated to obtain maximum oil extraction. However, Proir et al. (1991) discovered that preheating oilseeds before mechanical extraction can increase phosphorus concentrations in canola oil extruded. Cold pressed oils contained 13 ppm phosphorus while oil from heated seeds contained 64 ppm phosphorus on average. Oil degumming consisting of citric acid followed by hot water reduced phosphorus concentrations to 19 ppm in oil from heated seeds. They also suggested a correlation exists for non-triglyceride material in oil; as seed heating increased, phosphorus and FFA concentrations increased as well.

Smouse (1995) stated that expansion of seeds or introduction of steam increases the efficiency of oil extraction. Likewise, expansion may decrease lipase or phospholipase in soybeans, yielding oil with lower free fatty acid and less nonhydratable phospholipids. Likewise, Cvengros and Povazanec (1996) state that cold pressing is ideal for a farm level biodiesel operation. There is very little phospholipid output and the protein in the cake is not denatured, making it a good source for livestock feed ration supplementation.

2.4 Hydrolysis Issues

Hydrolysis in oilseeds that threaten the quality of biodiesel produced entails triglyceride hydrolysis. When the triglyceride molecule is oxidized, one, two or three free fatty acids are cleaved from a glycerol molecule. High FFA levels in vegetable oils, desired for transesterification to biodiesel, can prove expensive and intensive to treat and overcome so that a quality product is ultimately

produced. Hydrolysis can happen in oil at any stage of the process but the oil is most susceptible to hydrolysis after it is extruded from the seed.

2.4.1 Seed

Banks (1998) studied the effects of storage conditions on canola seed hydrolysis. He concluded that less than optimal storage conditions for canola can lead to, among others, increased FFA levels. Decreased temperatures and moisture content in storage facilities can ensure lower FFA concentrations in canola after they have been stored for the desired duration. He found that oil hydrolysis is dependent on storage temperature and relative humidity. At a storage temperature of 25 ^{o}C and a relative humidity of 70%, oil FFA would change by 1% in a 65 week time period. At storage temperatures greater than 30 ^{o}C there would be excessive FFA formation. FFA accumulation would be a direct result of triglyceride hydrolysis and is similar to hydrolysis experienced for frying oils. However, hydrolysis in frying oils is expedited due to substantially higher temperatures and hydrolysis of canola oil during seed storage at temperatures of 30 ^{o}C would occur considerably slower.

2.4.2 Vegetable Oil

Andersson and Lingnert (1998) researched the influence of oxygen and copper on the oxidation of rapeseed oil. They state that one of the most important factors to influence oxidation is metals in the oil and copper is most pro-oxidative. Also, storing oils in containers of materials other than glass and metals that do not have absolute barriers to oxygen will increase oil oxidation and hydrolysis of triglycerides. Similarly, Smouse (1995) indicated that factors affecting oxidative stability in vegetable oils include phospholipids, oil storage, fatty acid composition, light, anti oxidants, metals, and seed storage. In addition, Banks (1998) and Benjelloun et al. (1991) investigated oxidation effects due to metal traces. They demonstrated that metal traces (e.g. copper and iron) increase oxidation by catalyzing reactions

between unsaturated fatty acids and oxygen. Due to rapeseed oil's fatty acid content, it oxidizes rapidly as temperature increases. The removal of these metals can reduce oxidation.

In similar research, Rao and Artz (1989) researched the oxidative effects of extrusion temperature on corn meal/starch with soybean oil. They found that increasing the extruder temperature (115 ^{o}C to 175 ^{o}C) had decreasing effects on oil stability as well as metal contents, in particular iron. Metal contents have been shown to increase oxidation as well. Increased temperature tended to increase the back pressure in the extruder die, which suggested the source of the metal contents was from the extruder parts. Likewise, Wang and Johnson (2001) investigated qualities of soybean oil resulting from differing process methods. The found that extruded oil resulted in lower FFA values than solvent extracted oils. They attributed lower FFA levels to the rapid inactivation of lipases during extrusion.

Kucuk and Caner (2005) researched hydrolysis of sunflower oil as impacted by storage container material. Glass and polyethylenterephthalate (PET) were used as storage containers and samples were stored with and without exposure to light and air. Oil stored without air exposure and in the dark showed the lowest hydrolysis for both materials. However, less hydrolysis occurred in the oil stored in glass versus oil stored in PET because oxygen could permeate the PET. The combination of light and air exposure, regardless of the storage container material, had significant effects on hydrolysis of sunflower oil in this study.

Malcolmson et al. (1994) studied oxidative stability and shelf life of vegetable oils under accelerated storage at temperatures above 30^{o}C. They found that canola oil was more stable under lighted storage conditions than cottonseed and soybean oils, but less stable than sunflower oils. Canola oil is more prone to autohydrolysis than cottonseed oil at storage temperatures of 40 ^{o}C. Similarly, Przybylski et al. (1993) researched two varieties of canola oil. The canola oil with lower linolenic acid exhibited higher oxidative stability under accelerated storage conditions of 60 ^{o}C. For regular storage

conditions at room temperature that are not accelerated with elevated temperature, Martin-Polvillo et al. (2004) studied sunflower oils differing in unsaturation degree during long-term storage. They found that as the degree of unsaturation of sunflower oil increased, hydrolysis occurred at an increasing rate. These results correlate to saturation degree of oils studied by Malcomson et al. (1994).

If oils are high in unsaturation level, steps can be taken to prolong shelf-life and increase oxidative stability. Merrill et al. (2007) investigated oxidative stability of high-oleic (unsaturated) vegetable oils with and without antioxidants added. Among oils studied were soybean, corn, sunflower, high-oleic sunflower, canola, high-oleic canola, very high-oleic canola. Factors affecting the oxidative stability of vegetable oil include the fatty acid composition of the oil, antioxidants, oxygen, light, and storage temperature. Natural antioxidants, such as tocopherols, in oils increase oxidative stability. Likewise, Warner and Dunlap (2006) reported that extruded soybean oil may exhibit natural antioxidants as compared to hexane extracted soybean oils along with having natural ability to inhibit hydrolysis.

2.4.3 Biodiesel

Bondioli et al. (1995) investigated the storage stability of biodiesel by designing an experiment in which samples of biodiesel were stored in the dark, at two temperatures (20 ^{o}C and 40 ^{o}C), in both glass and iron containers with other samples exposed to increasing amounts of water. It was determined that, like vegetable oil, storing biodiesel at 20 ^{o}C decreases the potential for oxidation over a six month period. Even though oxidation was observed for samples stored at 40 ^{o}C with moisture exposure, it was minimal and the oil remained within technical specification. Biodiesel oxidation was dependent on container material and temperature. Storage in iron containers caused secondary oxidation, oxidation as a result of primary oxidation. Glass containers proved to be more favorable a storage containers than iron containers in terms of oxidative stability. Biodiesel storage in iron containers also had a tendency to

increase emission particulates derived from the storage container, however performance tests showed that storage containers had no significant effect on fuel performance in a diesel engine.

Bouaid et al. (2008) performed an oxidation stability study on biodiesel derived from rapeseed oil and bioethanol. They concluded that acid value, peroxide value and viscosity increased with an increased storage time and like Bondioli et al. (1995), recommended limiting the storage temperature and moisture content to avoid oxidation. Likewise, Dunn (2005) concluded that autooxidation can result in increased viscosity, acid value, and peroxide value.

In a long-term storage study, Mittelbach and Gangl (2001) investigated the stability of rapeseed and used frying oil biodiesels under varying conditions. They found that storing biodiesel in closed containers in the absence of daylight allowed for less hydrolysis than storing samples open to air and in daylight conditions. Likewise, Leung et al. (2006) researched the degradation of rapeseed biodiesel under different storage conditions. They found that biodiesel stored at temperatures less than 40 ^{o}C degraded minimally, while samples stored above 40 ^{o}C degraded as much as 40% within a 52 week period. They concluded that high temperatures in conjunction with air exposure greatly increased biodiesel degradation. Temperature or air exposure alone had little effect on biodiesel degradation. Water content in biodiesel contributed to degradation but to a lesser degree than the combination of temperature and air exposure. However, Thompson et al. (1998) studied long-term storage deterioration of methyl and ethyl esters derived from rapeseed oil. Samples were placed in glass and steel containers both inside and outside. Peroxide and acid values increased over a 24-month period with greatest increase experienced from 21 to 24 months.

Biodiesel does have the potential to oxidize as the research above shows. However, the shelf-life or storage can be extended and oxidation slowed by the addition of anti-oxidants. Tang et al. (2008) found that adding either natural or synthetic antioxidants to biodiesel increased storage life of the

product. In addition, Shahidi and Wanasundara (1994) reported that oxidative stability of canola oil treated with natural antioxidants was equivalent or superior to oil treated with synthetic antioxidants.

2.5 Biodiesel Production

2.5.1 Transesterification

There are different methods of producing biodiesel. Some work well for specific feedstocks, others work best for high ester conversion efficiencies, while others work best from a cost perspective. For the average Alabama farmer wishing to offset fuel expenditures by producing his own biodiesel from crops grown on-farm, cost of producing biodiesel is the most limiting factor that may extend his reliance on petroleum based products. A farmer who is able to buy petroleum fuel cheaper than he can make his own will obviously choose to do so.

There are two typical methods used in the transesterification process; base-catalyzed transesterification and acid-catalyzed transesterificaiton. Base-catalyzed transesterification can be conducted with, among other things, catalyst such as sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium methoxide ($KOCH_3$), or sodium methoxide ($NaOCH_3$). Acid-catalyzed transesterification can be carried out with, among other things, sulfuric acid (H_2SO_4), sulfonic acid (RSO_3H), hydrochloric acid (HCl). Both of these methods use alcohols, whether butyl, ethyl, or methyl alcohol. Many combinations and procedures at various concentrations exist that utilize these chemicals for biodiesel production. These amalgamations are associated with a wide range of costs, some of which may be cost prohibitive to farmers. Figure 2.1 illustrates the chemical formula of base catalyzed transesterification using methanol as the alcohol. A triglyceride reacts with three moles of alcohol, in the presence of a catalyst, to form three moles of esters and one mole of glycerol.

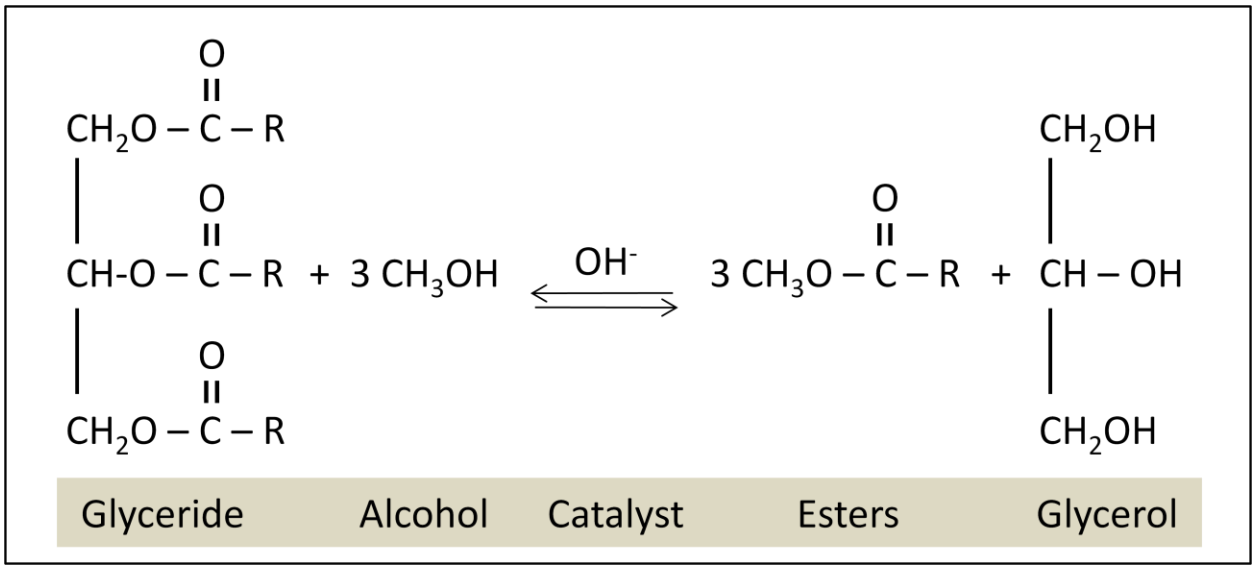

Figure 2.1. Chemical formula of transesterification.

Moser (2009) stated that biodiesel has many advantages and disadvantages. Among advantages are inherent lubricity properties, low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content, and lower exhaust emissions. Disadvantages mentioned included high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability, and potentially higher NO_x emissions.

2.5.1.1 Acid catalysis

Canakci and Van Gerpen (1999) suggested that biodiesel feedstocks containing high levels of FFA are complicated to transesterify with alkaline catalysts and soaps are likely to form. Soaps can prevent separation of the biodiesel from the glycerin fraction. They experimented with transesterification of food grade soybean oil. They compared the effect of different alcohol types (methanol, ethanol, 2-propanol, and n-butanol), molar ratios of alcohol to oil (3.3:1, 3.9:1, 6:1, 20:1, and 30:1), sulfuric acid catalyst amounts (1%, 3% and 5% by weight), reaction times of 48 and 96 hours, reaction temperatures of 60 ^{o}C, 75 ^{o}C, 110 ^{o}C, and 75 ^{o}C for methanol, 2-propanol, 1-butanol, and ethanol, respectively, and reaction temperatures of 25 ^{o}C, 45 ^{o}C, 60 ^{o}C with methanol as the alcohol in their study. Summarized results of their experiment include:

- A molar ratio of 30:1 and 20:1 resulted in 98.4% and 97% conversion, respectively.
- Ester conversion increased with temperature increase; 87.8% ester conversion at 60 ^{o}C.
- 72.7% to 95% ester conversion was obtained with 1% to 5% sulfuric acid, respectively.
- 96 and 48 hour reaction times resulted in 95% and 87.8% ester conversion, respectively.
- 88%, 93%, 92% and 95% ester conversion efficiencies resulted for methanol, 2-propanol, 1-butanol, and ethanol, respectively.
- Higher conversion rates were obtained by using higher reaction temperatures. Longer chain alcohols with higher boiling points allowed for the temperature increase.
- As little as 0.1 wt% water addition lowered ester conversion.
- More than 0.5 wt% water will lower ester yield to below 90%.
- 5 wt% water lowered ester conversion to 5.6%
- Base catalyzed transesterification with 3% water resulted in 90% ester conversion.
- FFA concentration above 5% resulted in less than 90% ester conversion.
- 5% FFA feedstock resulted in a solid soap mixture that prevented the separation of biodiesel from the glycerin fraction.

They concluded that factors affecting ester formation included molar ratio, reaction temperature, catalyst amount and reaction time. Acid catalyzed transesterification was much slower than alkali-catalyzed transesterification. Ester conversion was greatly affected by the molar ratio of alcohol to oil with acid catalyzed transesterification requiring larger amounts of alcohol for complete reactions. Reaction temperature just below the boiling point of the respective alcohol will result in greatest ester yield and ester formation increases with increased acid catalyst amount.

It is known that acid catalyzed esterification is more time consuming than base catalyzed transesterification. Freedman et al. (1984a) performed a similar study to Canakci and Van Gerpen (1999)

comparing molar ratios of 6:1, 20:1, and 30:1 for acid catalysis with methanol and 1% sulfuric acid. Ratios of 6:1 and 20:1 provided unsatisfactory conversion after 18 hours of reaction. A 30:1 molar ratio produced the highest conversion; previously discovered by Freedman and Pryde (1982). They also studied conversion effects as a result of different alcohols at temperatures just below their boiling points (60 ^{o}C, 75 ^{o}C, and 114 ^{o}C for methyl, ethyl, and butyl alcohols, respectively) and 1% sulfuric acid catalyst. The reaction times required to achieve satisfactory conversion were 2, 22, and 69 hours for butyl, ethyl, and methyl alcohols, respectively. Reaction temperature appeared to control conversion rate rather than alcohol used; also confirmed by Canakci and Van Gerpen (1999). Reaction temperature effects on conversion efficiency were confirmed by performing an experiment with each alcohol at 65 ^{o}C. After 69 hours, all experiments reached satisfactory conversion.

In instances where FFA is higher than 1.0%, Freedman et al. (1984b), Mbaraka et al. (2003), Zhang et al. (2003), Wang et al. (2005) recommended acid pretreatment. This process entails two steps where an acid catalyst in conjunction with methanol is first used to lower the FFA value and inhibit soap formation from a basic catalyst and FFA. Once the FFA concentration is lowered to within acceptable limits, ca. 1.0%, base catalyzed transesterification is used to complete the reaction.

2.5.1.2 Base catalysis

In addition to chemical combinations, one of the major variables affecting the biodiesel production process is FFA content. Predojevic (2008) found that biodiesel yield was inversely linked to acid value (FFA) and viscosity of vegetable oil. It has been reported that FFA concentrations greater than 3% decrease the ester conversion efficiency (Anggraini et al., 1999; Knothe et al., 2005). Canakci and Van Gerpen (1999) reported that FFA levels above 5% can lower ester conversion rate below 90% and that high free fatty acid feedstocks transesterified with a basic catalyst will form soaps that inhibit biodiesel separation from the glycerin fraction. However, Kemp (2006) detailed that oil with FFA levels above 1% require pretreatment. Some researchers emphasize that in vegetable oil containing more than 1% free

fatty acid, the acid catalyst will be much more effective than the alkali catalyst (Freedman and Pryde 1982; Freedman et al., 1984a; and Liu, 1994). However, Canakci and Van Gerpen (1999) also stated that transesterification with alkaline catalyst was more tolerant of water than with acid catalyst but acid-catalyzed transesterification is much slower than alkali-catalyzed transesterification. Likewise, Ballesteros et al. (1993) reported that base catalyzed transesterification aids in avoiding corrosion problems in engine components that are due to the presence of acid traces from acid catalysts. Of the scientists reporting experiments using base-catalyzed transesterification, Dorado et al. (2004) used KOH because it decreased ester forming reaction time; however, larger amounts of KOH are necessary due to is molecular weight. They also recommended basic catalyst to avoid the potential of engine corrosion caused by acid catalyst. Experiments were performed with canola oil using KOH and NaOH at room temperature. NaOH required up to 14 hour reaction time while KOH required only 1 hour reaction time at room temperature and 91.9% ester conversion was achieved using non-erucic canola oil with a FFA content of 2.2%.

Cvengros and Povazanec (1996) stated that the presence of water and high FFA will form soaps in a base catalyzed transesterification reaction. Soap formation consumes the catalyst and the reaction comes to equilibrium and stops. The glycerol phase was emulsified in the ester phase and separation was inhibited. A two step reaction can aid in overcoming this problem. By adding half the amount of alcohol and base catalyst, partial conversion was attained with less soap formation. The second step, adding the other half of alcohol and catalyst, completed the reaction with less susceptibility to reaction equilibrium.

2.5.1.3 Two Step Reactions

Kucek et al. (2007) investigated the possibility of two stage reaction. After two different single stage reactions with 12:1 ethanol molar ratio, 30 ^{o}C reaction temperature, 0.3 wt% NaOH and 1.0 wt% KOH, a second stage was added. Half the catalyst and molar ratio of ethanol were used for the second

stage as compared to the first due to lower amounts of unreacted glycerides. With NaOH, ester yield dropped from 97.2% to 96.3% and with KOH, ester yield dropped from 95.6% to 94.6%, however these yield losses were not significant. It appeared that no advantage was gained as a result of a second stage reaction.

The table in Appendix A.1 outlines varying biodiesel production techniques used in experimentation by different researchers. Some of the reported biodiesel yields were measured intermittently during the transesterification process and may not be the final ester yield obtained for the reaction. However, each provided valuable insight to better understand ester formation and the necessary procedures required to obtain satisfactory conversion.

2.5.2 Influences on Transesterification

2.5.2.1 Catalyst

A catalyst in the transesterification reaction is neither a product nor input of the reaction, but is meant to facilitate the reaction and push it to completion. Base catalysts in the transesterification reaction also serve a dual purpose as they neutralize FFA that otherwise may impede the reaction. Feuge and Gros (1949) and Lehman and Gauglitz (1966) found a base catalyst also has the potential to influence glycerol yield from the biodiesel, which in turn, dictated ester conversion; tying the catalyst back to is fundamental purpose. Results from their study indicated that glycerol yield, when transesterifying peanut oil, was 77% and 95% for 0.2 wt.% and 0.8 wt.% sodium hydroxide, respectively with a 6:1 molar ratio of methanol to oil. This catalyst amount is lower than the generally accepted amount of one percent by weight used by most researchers and illustrated the necessity for higher catalyst amount recommendations.

Kucek et al. (2007) investigated the differences in NaOH and KOH as catalysts in transesterifying soybean oil with a molar ratio of ethanol to oil of 12:1, reaction temperature of 70 ^{o}C, and reaction time

of one hour. More KOH (40%) was used in comparison to NaOH to account for difference in molar mass. KOH of 0.42 wt% led to no phase separation, however at 1.4 wt.% KOH yield losses were apparent stemming from soap formation. One wt.% KOH was then used. It was determined that KOH resulted in lower ester yields as opposed to NaOH and was attributed to moisture in KOH.

Singh et al. (2006) investigated process optimization of biodiesel production using alkaline catalysts with canola oil and methanol. They studied, sodium hydroxide, potassium hydroxide, sodium methoxide, and potassium methoxide at molar ratios to canola oil of 0.1, 0.2, and 0.3 in order to develop an optimization model. The reaction temperature was varied from 40 – 60 ^{o}C and the reaction time was 10 minutes. They determined that potassium based catalysts gave better ester yields than sodium based catalysts and methoxide yields gave highest conversions. Highest conversion efficiencies were attributed to the fact that methoxide was theoretically free of water. In the formation of methoxide from methanol and hydroxide when mixed simultaneously with oil feedstock, some water was formed which consumed a portion of the catalyst. However, more potassium based catalyst was required for the reaction because of its elevated molecular weight as compared to sodium based catalyst and potassium based catalysts have greater tendency to form soap. They also stated that strong emphasis should be placed on the catalyst molar ratio to feedstock as molecular weight varies among alkali catalysts; most researchers use weight percentage, typically 1 wt.%, when transesterifying oil feedstocks with alkali catalysts. Their optimization model resulted in 99% conversion using 1.59 wt.% $KOCH_3$, 4.5 molar ratio of methanol to canola oil, 50 ^{o}C reaction temperature and 10 minute reaction time. The model had an R^2 value of 0.85 and when tested resulted in 95.8% ester yield.

2.5.2.2 Water

Wright et al. (1944) found that as little as 0.3% water could reduce ester conversion by consuming the catalyst necessary for the reaction. Bradshaw and Meuly (1944), Bradshaw (1942), and Feuge and Gros (1949) reasoned that limiting water content to less than 0.5% is imperative for

satisfactory ester conversion. Likewise, Canakci and Van Gerpen (1999) reported that ester formation was greatly retarded by the presence of water. Less than 0.5% water was recommended for best conversion. FFA in vegetable oil can have a significant impact on transesterification. If base catalyst was used the water formed as a result of the base catalyst introduction to the FFA can inhibit the reaction as well as soaps formed. FFA concentrations greater than 5% resulted in ester yields less than 90%. Similarly, Freedman et al. (1984a) stressed that when using sodium methoxide or hydroxide as a transesterification catalyst, both should be kept in an anhydrous form. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide and Kucek et al. (2007) attributed low ester conversion to water in KOH catalyst noting that NaOH was less susceptible to water than KOH.

2.5.2.3 Alcohol

Another important variable of biodiesel production affecting the yield of esters is the molar ratio of alcohol to vegetable oil employed (Freedman and Pryde, 1982; Canakci and Van Gerpen, 1999). In acid-catalyzed transesterification, a higher molar ratio of alcohol to oil is required than that of alkali-catalyzed. The most frequently used alcohols are butyl, methyl, and ethyl alcohols at molar ratios ranging from 3.3:1 to 30:1. These alcohols vary in price and performance characteristics. Bradshaw and Meuly (1944) and Bradshaw (1942) stated that a 4.8:1 molar ratio of alcohol to oil resulted in 98% conversion and if added in three or four portions, the molar ratio could be reduced to 3.3:1 with similar results. Bradshaw and Meuly (1944), Bradshaw (1942), and Freedman and Pryde (1982) also found that molar ratios greater than 5.25:1 and 6:1, respectively, interfered with gravity separation of the glycerol and added unnecessary cost. Higher conversion rates were found for the longer chain alcohols as compared with methyl ester and are probably due to the higher reaction temperatures allowed by their higher boiling points. This effect apparently dominated any decrease in reaction rate associated with the longer chain alcohols. Butyl alcohol exhibited the shortest reaction time in the biodiesel production

process as compared to ethyl and methyl alcohol because higher temperatures were used but after one hour, the conversions were about the same.

Dorado et al. (2004) suggested that transesterification of canola oil can be performed with 1.4% KOH, 4.6:1 molar ration of methanol to oil at 20-45 ^{o}C and 30 minutes of stirring. They suggested that a greater amount of KOH reduced the amount of required methanol. However, there was an optimal level of each constituent, if lower or higher concentrations of methanol or KOH were used, soap formation or incomplete reaction occurred. Therefore, they recommended lower amounts of methanol be used compared to other researchers but this reduction was due to higher concentration of KOH in the reaction. However, methanol amounts of 20 wt.% made glycerol separation difficult, thus decreasing ester yield. They also discovered that methanol amounts up to 10% produced two layers, a lower gelatinous layer and an upper opaque layer. This amount of methanol was insufficient to perform complete transesterification.

The generally accepted molar ratio of alcohol to oil is 6:1. Freedman et al. (1984a) found that a this molar ratio of methanol to oil resulted in 98% ester conversion at a 60 ^{o}C reaction temperature, one hour reaction time, and 0.5% sodium methoxide catalyst. At 3:1 molar ratio, the ester conversion was reduced to 82%. High ester conversion (93% - 98%) was observed for soybean, sunflower, peanut, and cottonseed oils at 6:1 molar ratio of methanol to oil. They also experimented with ethanol, butanol, and methanol at molar ratios of 6:1 and 3:1 at temperatures just below the boiling points of each respective alcohol and 0.5 wt.% sodium methoxide. All ester conversion at 6:1 molar ratio was similar after one hour (96% - 98%). For 3:1 molar ratio, butyl alcohol reaction was at 88%, while ethyl and methyl were at 81% and 82%, respectively. Excess alcohol was needed for satisfactory reaction.

Kucek et al. (2007) experimented with ethanolysis of soybean oil. The experiment was conducted with molar ratios of ethanol to oil of 6:1 and 12:1, NaOH concentrations of 0.3 wt% and 1.0 wt%, and reaction temperatures of 30 ^{o}C and 70 ^{o}C. No phase separation was observed at a molar ratio

of 6:1, NaOH of 0.3 wt% and reaction temperatures of 30 ^{o}C or 70 ^{o}C, due to the low alcohol and catalyst content. Highest ester yields in a single phase reaction, 96.8% and 97.2%, were observed at 12:1 molar ratio and 0.3 wt% catalyst at, 30 ^{o}C and 70 ^{o}C, respectively. Ester yields beyond 98% were achieved with a two stage reaction.

2.5.2.4 Reaction Temperature

Reaction temperature can dictate the reaction duration according to Canakci and VanGerpen (1999) with optimal temperatures ranging a few degrees below the boiling point of the respective alcohol used for shortest reaction times. Dorado et al. (2004) found that transesterification of canola oil with 1.4% KOH and 16 vol.% methanol was achieved at room temperature after one hour, while transesterification with NaOH took up to 14 hours to complete at room temperature. However, Trent (1945) found that reaction temperatures greater than 60 ^{o}C should be avoided because they tended to accelerate saponification of glycerides by basic catalysts.

Freedman et al. (1984a) found that transesterifying cottonseed, peanut, soybean, and sunflower oils with either sodium hydroxide or methoxide with 6:1 molar ratio of methanol, ethanol, or butanol to oil and a reaction temperature of 60 ^{o}C resulted in complete conversion after 1 hour. At a moderate temperature of 32 ^{o}C, oils were transesterified after 4 hours, slightly exceeding the conversion at 45 ^{o}C and 60 ^{o}C. Freedman et al. (1984a) and Canakci and Van Gerpen (1999) determined that best conversion was achieved at reaction temperatures just below the respective alcohol's boiling point.

2.5.2.5 Reaction Time

Dorado et al. (2004) found that transesterification of canola oil with 1.4% KOH and 16 vol.% methanol was achieved at room temperature after one hour, while transesterification with NaOH took up to 14 hours to complete at room temperature. Similarly, Freedman et al. (1984a) found that at a molar ratio of 6:1 methanol to oil, 80% of the oil was converted to ester after only one minute of

reaction for soybean and sunflower oils. However, under the same conditions, only 55% of peanut and cottonseed oil were converted to ester. After one hour, the conversion efficiency for all four oils was 90% or higher with cottonseed oil being the lowest at 90%. On the other hand, after only 10 to 15 minutes, Canakci and Van Gerpen (1999) suggested that ester conversion is near completion with basic catalysts and various alcohols. When using acid catalysts, reactions may take up to 48 to 96 hours for satisfactory conversion. Most published biodiesel production literature recommended one hour reaction time for base catalyzed transesterification reactions.

2.5.2.6 Glycerol Settling Time

Dorado et al. (2004) found that a settling time of 1-3 hours was sufficient to achieve satisfactory phase separation of glycerol and methyl ester at a temperature of 38 ^{o}C. When the temperature was lowered by 10 ^{o}C to 15 ^{o}C, several days were required to achieve satisfactory phase separation. In the event settling temperature and time was low and took several days, respectively, the opaque ester samples turned crystalline and a slight glycerol lower phase appeared. They suggested that glycerol was more soluble at lower temperatures and does not fully separate.

2.5.3 Refining Crude Biodiesel

For a quality end product, biodiesel must be refined to remove impurities and excess catalyst and glycerol. Washing is most often used in published literature as a means to refine biodiesel and can be performed with water (water washing or wet washing) or a resin (dry washing). However, Kucek et al. (2007) used Magnesol®, a commercial adsorbent, to purify biodiesel. It was a synthetic amorphous magnesium silicate that removes contaminants such as water, soaps, free glycerin, and unreacted glycerides. They found that two wt% Magnesol® eliminated the need for water washing and generated a product with low unreacted glycerides. The only drawback; Magnesol® was not recyclable and

procedures for its disposal were unclear. However, it virtually eliminated the usage of water and water washing in the biodiesel production process.

Predojevic (2008) experimented with purifying biodiesel with different products. He used silica gel, 5% phosphoric acid, and hot distilled water and a two step alkali transesterification reaction with waste sunflower oil. For the silica gel purification, a column was designed and silica gel was added (3 g). A top layer of anhydrous sodium sulfate was added to remove any traces of water (3.14 cm^3). Purification of 200 g of methyl ester with 5% phosphoric acid was performed by washing the crude biodiesel with 50 cm^3 of a 5% phosphoric acid/water solution up to 7 times until reaching a neutral pH after which the biodiesel was dried with sodium sulfate. Hot distilled water was used in a third purification experiment. 50 cm^3 of water was used to wash the biodiesel up to 10 times after which the biodiesel was dried with sodium sulfate. The results indicated that silica gel and phosphoric acid gave higher ester yields than hot water washing. However, the purity of biodiesel using all three prescriptions was similar. Lower yields due to water washing were attributed to the number of washings required (10) to reach neutral pH.

2.6 Economic Analysis

Economics of the biodiesel production process can be studied from several angles. Obviously the financial element is important from a small-scale production standpoint, but net energy return of biodiesel compared to other fuels is also a parameter of significant interest. Cvengros and Povazanec (1996) stated that the energetic output of rapeseed methyl ester ranged from 2.5:1 to 3.5:1, while the energetic output for ethanol is only 1.63:1. However, net energy production of one hectare of rapeseed crop is 76 GJ for methyl ester and 160 GJ for ethanol. They also advocated for a small production plant in which a farmer can take his crop. The crop is converted into biodiesel and cake and returned to the farmer for use as fuel and livestock feed supplementation, respectively. The advantage of this process,

according to Cvengros and Povazanec (1996), was that continuous production was not required, it was performed on a supply basis. This system was a low cost investment, allowing for rapid implementation, and cost savings on transportation. In contrast, a large production system is better equipped to control fuel quality, production quality, and byproduct employment. According to Cvengros and Povazanec (1996), alternative fuels, such as rapeseed methyl ester, reduce environmental impacts of transportation, reduce the dependence on crude oil imports and ease political and economic factors. Rapeseed based biodiesel offered business possibilities to agricultural enterprises for periods of excess agricultural production, they allowed economic uses of devastated soils, and were a low-waste technology generating no by-products with environmental impact. However, Paulson and Ginder (2007) and Reka-Schill (2008) stated that feedstock acquisition currently accounts for over 80% of biodiesel production expenses, resulting in a serious threat to the economic viability of the biodiesel industry.

Moser (2009) reported that desirable characteristics of alternative oilseed feedstocks for biodiesel production included adaptability to local growing conditions (rainfall, soil type, latitude, etc), regional availability, high oil content, favorable fatty acid composition, compatibility with existing farm infrastructure, low agricultural inputs (water, fertilizer, pesticides), definable growth season and uniform seed maturation rates. These desirable characteristics would also include potential markets for agricultural by-products, and the ability to grow on agriculturally undesirable lands, and/or in the off-season from conventional commodity crops. Biodiesel fuels prepared from feedstocks that meet at least a majority of the above criteria would hold the most promise as alternatives to petrodiesel.

A major destabilizing factor that producers faced in 2007 which led to an unstable market was biodiesel feedstock prices (soybeans) (Crooks, 2008). He indicated that soybean oil prices were only 44 cents per kilogram not long ago but endured a 160% price increase from 2005 to 2007. This price increase was attributed to decreased soybean production acres as a result of increased demand for corn. Many biodiesel production facilities have closed and are for sale. The ones that are operational are

only at 20% capacity. However, biodiesel exports were at an all-time high with 80% of biodiesel produced in the US being exported.

Crooks and Dunn (2006) stated that although great interest exists for renewable fuels, it is unlikely that there will be a shift toward production in the southern US in the near future. As of 2008, there existed a small agri-biodiesel producer tax credit which subsidized small-scale, on-farm biodiesel production at 2.6 cents per liter. This credit is available to producers for their first 57 million liters per year produced but not applicable when producing more than 227 million liters per year. They also mentioned that there existed hope of biodiesel becoming a preferred lubricity solution to the EPA's regulation of ultra low sulfur petrodiesel which requires lubricity additives to overcome the absence of sulfur.

Increased employment and value-added economic activity could arise as a result of biodiesel plants established in rural economies (Gustafson, 2003). Biodiesel plants that utilize minor oil crops as their feedstock source could yield comparable increases in economic activity. Economic feasibility in terms of investment costs were around $0.26 per liter but increase proportionally with plant capacity because ease of production limits economies of scale. Costs of production are decreasing due to increased plant efficiency and conversion but still pale in comparison to $0.05 to $0.13 per liter production costs of petrodiesel. In conclusion, he stated that production costs, like ethanol, were expected to decrease as a result of increased efficiency and innovations in production techniques. Favorability may also lie in consumers who wish to purchase biodiesel for its environmental benefits and potential to lessen strains on climate change. However, these consumers may typically be in more densely populated areas where feedstock production was displaced requiring transportation of the biodiesel and increased overall cost.

Kenkel and Holcomb (2006) stated that geographic concentration for ethanol plants in the mid-west has been driven by feedstock availability and the lack of need for transportation when considering

ethanol production. Similarly, biodiesel plants have been located near crushing facilities in soybean-rich areas. Van Dyne and Raymer (1992) are in agreement as they see largest production potential of biodiesel with integrated systems in grain or feed handling and processing facilities. But, market forces are lessening the need for these geographic restraints. The implementation of train transport of feedstocks in conjunction with lower utility costs and plants utilizing co-products of the transesterification process are negating the need for biodiesel production plants to be located in traditional venues and newly built plants in alternative locations are beginning to experience close competition with traditionally located biodiesel production plants. Kenkel and Holcomb (2006) also rationalized that plant locations near co-product utilization facilities were favorable. The most common co-product from the transesterification process is oilseed meal. The oilseed meal accounted for 60% to 80% of the initial oilseeds used depending upon the feedstock. These meals were highly desired for both ruminant and non-ruminant livestock protein sources in feed rations. By products directly from transesterification, namely glycerin, are highly valued for soap production and also development of films and casing materials. Favorably for biodiesel plants, as opposed to ethanol plants, was the relatively low consumption of utilities such as electricity and natural gas. However, this advantage is negated when considering the vast amount of utilities requirement for the oilseed crushing process.

Kenkel and Holcomb (2006) also investigated economics of on-farm or small-scale oilseed processing and biodiesel production. Table 2.1 highlights their research of breakeven oilseed costs at various biodiesel prices. They concluded that small-scale crushing and biodiesel production was marginally feasible and that on-farm biodiesel production was not feasible at current prices. However, the pricing structure used in their research was that of 2005-2006 actual costs a farmer would incur. Returns were sensitive to the farm level price of commodities, biodiesel, and meal value. On-farm processing of oilseed higher in oil content (canola, sunflower) was marginally feasible, but feasibility of soybean based biodiesel required a biodiesel value above $1.32/liter with historically high meal prices.

Table 2.1. Breakeven oilseed crop values at various biodiesel prices. (Kenkel and Holcomb, unpublished data).

Biodiesel Price	$2.50	$2.75	$3.00	$3.25	$3.50
Breakeven Canola Price ($/kg)	$0.181	$0.214	$0.249	$0.287	$0.322
Breakeven Sunflower Price ($/kg)	$0.163	$0.201	$0.238	$0.276	$0.315
Breakeven Soybean Price ($/kg)	$0.195	$0.221	$0.246	$0.272	$0.298

In potential opposition to biofuel production plants, commodity groups in grain-deficit areas fear that increased production costs and decreased production of their respective crops may result. The Oklahoma Wheat Growers' Association opposed a canola processing/biodiesel plant in OK because it had the potential to decrease wheat acres. The fact that cropping shifts or experimental crops for bioenergy production often incur lag time in adoption and production of sufficient crop acreage, making it extremely difficult to justify bioenergy production plants in some areas with so much inherent uncertainty. It is difficult to establish a plant without sufficient production of the needed feedstock(s); likewise it is also hard to justify cropping changes without a production plant or subsequent market for the crop.

Because the price of soybean oil, prior to transesterification, is higher than petrodiesel, Raneses et al. (1999) found that biodiesel had not penetrated the petrodiesel market in the US. One possible solution they suggested was similar to Crooks and Dunn (2006), in which biodiesel can be used as a fuel additive in concentrations of 1% to 3% by volume to enhance fuel performance. They suggest that petrodiesel fuel additives currently used cost more than biodiesel but biodiesel out performs these additives in terms of cetane number and lubricity and the real market potential of biodiesel may lie in this sector.

Van Dyne and Raymer (1992) made a statement that biodiesel feedstock can possibly be grown on land that the US government currently holds idle annually to normalized supply and demand of food crops. In the southeast region of the US, there are a total of 3.5 million hectares held idle annually and some acreage is the result of a 10-year Conservation Reserve Program (CRP). Large volumes of biodiesel

could be produced from this land. These researchers investigated the potential of growing canola on this land and estimated that an average of 2.4 billion liters of biodiesel could be produced annually and if maximum yields were experienced, 3.2 billion liters could be produced in one year.

Using several methods and several feedstock avenues, Zhang et al. (2003) conducted a sensitivity and economic feasibility analysis of biodiesel production. They concluded that alkali-catalyzed transesterification from virgin oil had the lowest capital investment because of relatively small infrastructure requirements, but had the highest manufacturing cost. Likewise, virgin oils were higher priced than waste vegetables oils (WVO) previously used in frying. Zhang et al. (2003) found that the pretreatment of WVO in a base catalyzed reaction negated the savings from the low cost oil itself. They determined that acid-catalyzed transesterification was the best option in terms of economics and the glycerin co-product could offset production costs by as much as 10% annually. Sensitivity analysis showed that plant capacity, price of WVO, and price of biodiesel were major factors affecting the economic feasibility of production.

Paulson and Ginder (2007) stated that rapid growth in the biodiesel industry caused many recent studies to become obsolete within months of plant completion. The estimates these researchers studied, 115 million and 230 million liter per year plants, differed by 0.37 cents per liter of production cost with biodiesel from the 230 million liter per year plants costing less per liter to produce. These savings came from marginal labor costs and capital costs. They speculated that increasing returns to scale may provide larger scale plants with an advantage in terms of bidding for scarce high-quality virgin feedstocks. Since almost 85% of the total operating expenses were tied up in feedstock, this bidding advantage established whether a plant continued to operate or shut down. Smaller plants with variable operating costs would be forced to shut down in these scenarios. However, in 2007 there were no plants operating at 230 million liters per year capacity and the authors stressed that these theoretical estimates are extrapolated from real data for a 115 million liter per year plant and need to be

interpreted with caution. The researchers also stress that the quality of biodiesel produced from non-virgin feedstocks can be highly variable and costs can range widely making profit margins difficult to ascertain for these type plants.

2.7 Effects of Microorganisms in Biodiesel Storage Tanks

Whether petroleum-based fuel or bio-based fuel is stored long term, contamination from water is a major issue in storage tanks and can potentially lead to microbial growth. With petroleum-based fuel, water contamination is minor as petroleum fuel has little affinity for water. Van Gerpen et al. (1996) found that biodiesel has a water saturation level of approximately 1,500 ppm, nearly 40 times higher than petroleum diesel. When water is introduced to a storage tank through vents, seals, openings in the tank, or from humidity in the atmosphere, it collected in the bottom of the tank upon saturation of the fuel. ASTM standard D 6751 (2007) requires that biodiesel not contain more than 500 ppm dissolved water, but the introduction of water during transport and storage is almost inevitable and biodiesel will absorb 1,200 ppm to 1,500 ppm. However, because this amount of water will be bound to the biodiesel and is not free water, it is not available for microbial growth. Because of the water saturation limit of biodiesel, any additional water in the tank will collect in the bottom of the tank and can potentially lead to microbial growth. Water collection at the bottom of the storage tank, coupled with biodiesel's biodegradability, allows for microbial growth if good "house-keeping" practices are not followed. Biodiesel has increased bioavailability to microorganisms such as strains of *Pseudomonas* as compared to petroleum diesel. In terms of fuel spills, degradation of biodiesel from microbial growth may have a positive impact on the environment as compared to petroleum diesel but a negative impact on fuel stability during storage.

Van Gerpen et al. (1996) researched treatment methods for reducing microbial growth and found they can include periodic removal of water that collects in the bottom of storage tanks, transport

and storage of biodiesel in separate infrastructure from petroleum diesel that is completely sealed, or the addition of biocides. However, biocides can have an adverse effect on the biodegradability of biodiesel. Van Gerpen et al. (1996) also recommended that biocides should be added to biodiesel not used within a short period of time to inhibit mold growth in the storage tank.

2.7.1 Biodiesel Storage

2.7.1.1 Storage Temperature

Biodiesel is more susceptible to microbial growth because of its biodegradability as compared to petroleum diesel. A study by Williamson and Badr (1998) showed that biodiesel degraded over 98% biologically within three weeks while petroleum diesel degraded only 50% during the same time period. One component effecting degradation of biodiesel is storage temperature. Leung et al. (2006) reported that storage temperatures of 40 ^{o}C had the largest degradation impact on biodiesel (Figure 2.2). This degradation was especially evident when biodiesel was stored in an unsealed container. Biodiesel stored at lower temperatures in sealed containers, whether water was present not, showed the lowest degradation rates. However, there existed little differences among samples stored in sealed conditions, irrespective of temperature. They concluded that high temperature, coupled with air exposure, led to increased degradation rates of biodiesel due to oxidation.

2.7.1.2 Water Contamination in Biodiesel

Once a vegetable oil or animal fat feedstock has been transesterified, it must be purified. Purification of biodiesel can be performed in several ways and is necessary to remove excess glycerol, unused catalyst, and soaps that may have formed during transesterification. Water-wash purification is one technique sometimes used that entails spraying water through the biodiesel. Because water is denser than biodiesel, it settles to the bottom of the washing vessel and can then drained off but some water may be retained in the biodiesel. Biodiesel is hydrophilic indicating its ability to absorb water it

may come in contact with. According to Van Gerpen et al. (1996), biodiesel has the ability to absorb up to 1,500 ppm of water. ASTM standard D 6751 (2007) outlines that biodiesel contain no more than 500 ppm water. This method will require further energy input to "dry" the biodiesel in order to meet ASTM standard D 6751 (2007). If biodiesel is water-washed and not dried, there exists potential for it to contain excessive amounts of water and even free water. Upon storage, free water will collect in the bottom of the vessel and introduce an environment for microbial growth.

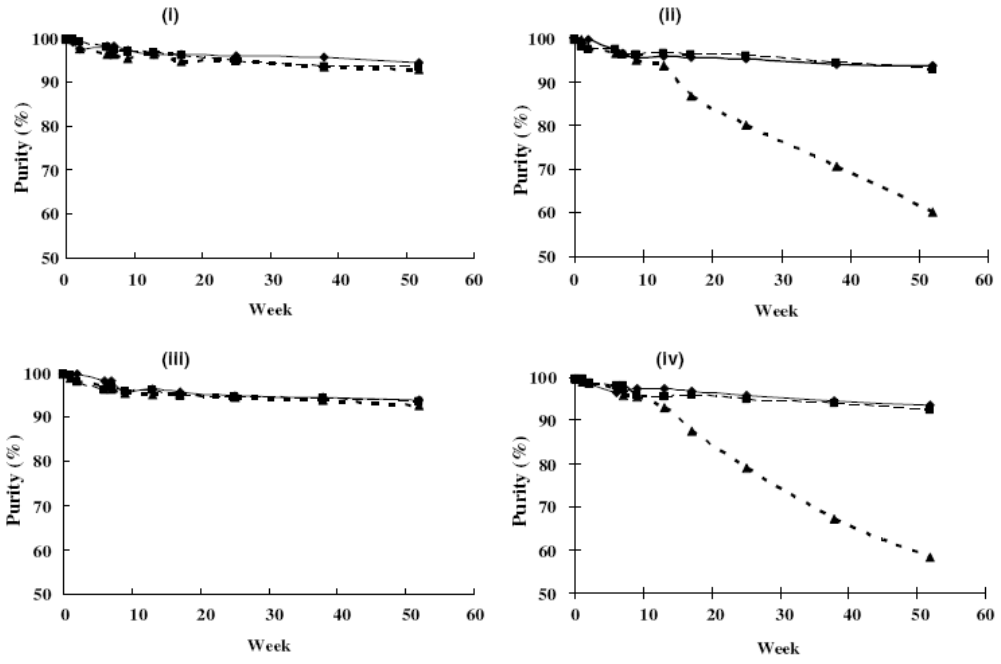

Figure 2.2. Purities of biodiesel degradation at different temperatures.
(i) sealed, (ii) with air exposure, (iii) sealed with water presence, (iv) with air exposure and water presence. (♦) 0 °C; (■) 20 °C; (▲) 40 °C. (Leung et al. 2006).

Further, biodiesel is hygroscopic in nature and can absorb moisture from the air. Once biodiesel has reached saturation capacity from water washing, moisture from the air or contact with water from another source, excess water above 1,500 ppm will accumulate in the bottom of the storage tank due to its dense nature compared to biodiesel. Therefore, water can be present in biodiesel storage tanks in two forms, free water or dissolved water. Dissolved water in biodiesel is not readily available for microbial growth, however free water existing in a biodiesel storage tanks provides a conducive

environment for microorganism growth. On the other hand, biodiesel may be dry-washed with resins such as AMBERLITE™ BD10DRY™. Dry washing with a resin provides a "water free" process thereby reducing the potential of initial water contamination in a storage tank.

In addition to storage temperature affecting biodiesel degradation, it can also affect water solubility into biodiesel. Van Gerpen et al. (1996) studied water solubility as a result of different biodiesel and petroleum diesel temperatures. At 25 ^{o}C, they found that 60 ppm of water will be absorbed into petroleum diesel fuel. The water saturation level for biodiesel was observed to be 40 times greater, or approximately 1500 ppm, than petroleum diesel. Table 2.2 illustrates these findings. Likewise, efforts by He et al. (2007) recommended underground storage tanks for biodiesel as they maintained a relatively constant temperature that lessens temperature effects on moisture absorption. Figure 2.3 illustrates findings of He et al. (2007) for biodiesel and petroleum diesel (D2) saturation levels at different temperatures. They concluded that no significant differences existed for biodiesel from different feedstocks tested: soybean, canola and mustard. Of interest, they discovered that as temperature increased, moisture content increased at a rate of 22.2 ppm/^{o}C. They speculated that biodiesel absorbs moisture as the temperature rises, then the moisture precipitates as the temperature falls. If the temperature in the storage tank oscillates, water accumulation in the tank bottom can result and provide sufficient media for microbial growth. Burkhalter (1976) studied similar storage effects on oil and agreed with these findings, suggesting that tank sweating caused moisture to drip into the oil and resulted in an effective degumming process. However, unwanted solids did accumulate in the tank bottom. This would most likely not be the case with biodiesel, but a water washing effect may take place. In the event biodiesel was not previously washed effectively, unwanted glycerol, soaps, etc may accumulate in the tank bottom.

Table 2.2. Water contents (ppm) in various fuels and blends after vigorous mixing with water for various periods at 25 °C. (Van Gerpen et al., 1996)

	0 HR	1 HR	3 HR	18 HR	1 D	5 D
Methyl soyate (PV=124, Interchem)	0	0	0	0	-	-
Methyl soyate (PV=20)	37 c	1460 a	1595 a	-	1255 b	1225 b
20% Blend (PV=20)	40 a	37 a	38 a	-	33a	45 a
Diesel fuel (No. 2)	28 a	-	81 a	30 a	-	-

*Values are the average of duplicate measurements.
Values with different superscript in the same row are significantly different at α=0.05.

Water can enter a storage tank through vents, seals, or openings. It may be necessary to avoid using current petroleum diesel storage infrastructure to ensure biodiesel is kept free of water. On the other hand, good house-keeping measures can be taken to reduce water contamination and thereby the potential for microbial growth. Periodic draining from the bottom of the tank will ensure free water is removed. Sealing the tank and replacing degraded fixtures may aid in preventing moisture from seeping into the tank.

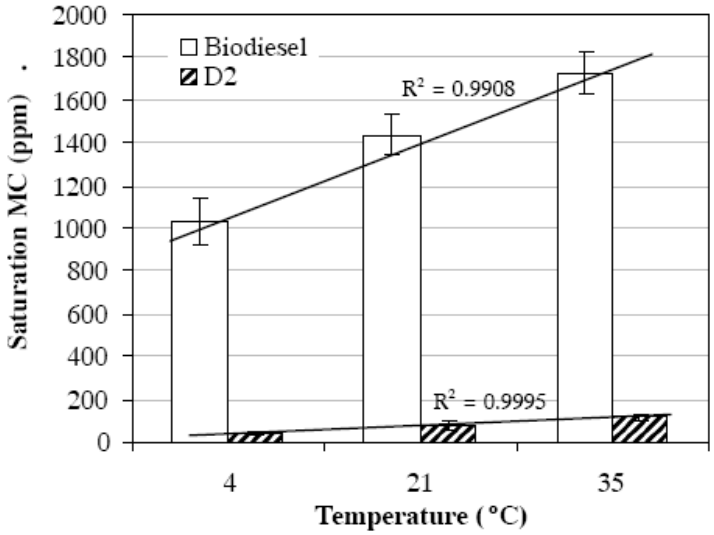

Figure 2.3. Saturation MC of biodiesel and diesel at three temperatures. (He et al., 2007)

In addition to engine corrosion problems, water in biodiesel can facilitate microbial growth. Van Gerpen et al. (1996) found that species of yeast, fungi, and bacteria can grow at the interface between biodiesel and free water in a storage tank. These organisms can produce sludge and slimes that can

cause fuel filter plugging. Some organisms can even convert sulfur in fuel to sulfuric acid resulting in corrosion of metal storage tanks although ASTM standard D 6751 (2007) states that no more than 500 ppm sulfur is allowed in biodiesel.

2.7.2 Microbial Growth

In the same study by Van Gerpen et al. (1996) outlined above, a microbial growth experiment was conducted. Samples of methyl soyate and petroleum diesel fuel were tested with various nitrogen sources (Yeast N-base and *Pseudomonas* basal mineral N-base). Carbon sources used were No. 2 diesel fuel and methyl soyate with microbial growth compared. The culture media was incubated in the dark at room temperature while microbial growth was assessed using a spectrophotometer testing for optical density. The yeast in a 1% biodiesel sample showed no significant growth until day 6, after which visible mold was detected. However, the 1% petroleum diesel fuel showed signs of mold growth only 3 days after inoculation. Pseudomonas produced growth in biodiesel after only 2 days and development in petroleum diesel after 3 days. The cultures from biodiesel and petroleum diesel contained different morphologies indicating different types of microbial growth. However, two cultures were the same morphology for both biodiesel and petroleum diesel. Table 2.3 highlights results from this study and it was evident that Pseudomonas grew approximately 70 times faster in biodiesel than petroleum diesel within 6 days.

Short to medium length hydrocarbons were greatly affected by strains of *Pseudomonas aeruginosa*, *Bacillus sp*. and *Micrococcus* in comparison to longer chains. Ghazali et al. (2004) and Lazar et al. (1999) reported that these strains indicated effectiveness in degrading hydrocarbons. However, Schleicher et al. (2009) reported that blends of petroleum diesel and biodiesel showed strong hydrocarbon degradation. B20 exhibited strongest microbial growth as compared to B5 and B100. Microbial growth experienced in B20 was 1700 times higher after 84 days of incubation than at the commencement of the experiment. However, B100 and B5 blends only experienced microbial growth of

13 and 20 times higher than initial measurements, respectively. Nonetheless, microorganism population was dependent on the concentration of petroleum diesel and was highest for B5 at 80%. Under anaerobic conditions, microorganisms in B100 grew better at 37 ^{o}C as compared to B5 and B20 blends in which microorganisms grew better in aerobic conditions. Highest levels of sedimentation as a result of microbial activity were experienced in B20. Less was measured in B5 and no sediment formed in B100.

Table 2.3. The growth of microorganisms on various diesel and methyl soyate liquid media. (Van Gerpen et al., 1996).

	Absorbance			
Liquid media	1 day	2 days	3 days	6 days
Yeast N + methyl ester	0.016	0.023	0.030	0.009
Yeast N + diesel	0.042	0.067	0.250	0.448
Pseu N + methyl ester	0.057	2.004	4.700	10.240
Pseu N +diesel	0.038	0.073	0.177	0.147

*The data reported in the table are the optical densities measured by the spectrophotometer at 520 nm.

Research by Ryu et al. (1996) suggested that bacteria and molds that grow in petroleum diesel fuel storage tanks in the aqueous phase are different than microorganisms that are found in biodiesel storage tanks. Similar to biodiesel storage tanks, these bacteria and molds grow on the interface between the fuel and water and can form large populations of biomass. However, Ryu et al. (1996) states that methyl soyate may inhibit microorganisms that can grow in petroleum diesel fuel storage tanks. They speculated that the unsaturation level of the oil plays an integral role in inhibiting microbial growth in petroleum fuel storage tanks. However, a side-by-side comparison of this study with results by Van Gerpen et al. (1996) cannot be made because different bacteria were used.

2.7.3 Environmental Impacts

In terms of using biodiesel for fuel, microbial activity and degradation negatively impacted its intended purpose. However, as outlined by Hill (2008) it could hold positive implications for the environment in the event of a fuel spill. Bioremediation of soil or a water system contaminated by biodiesel may require minimal attention as compared to the site of a petroleum diesel spill. Likewise, biodiesel constituents are natural and less harmful than constituent of petroleum diesel.

2.7.4 Biodiesel Storage Stability

Prevention of microbial growth by the eradication of free water or inhibition of water ever contacting biodiesel would be the most preferred method of ensuring biodiesel integrity. However, this is not always possible. To impede microbial growth in biodiesel, biocides may be recommended. On the other hand, Hill (2008) stated that biocides added to a tank currently experiencing heavy microbial activity may make the situation worse. In this case, biocides can lead to increased levels of particulates in the fuel inevitably causing downstream issues in other fuel tanks or engines. Hill (2008) also implied that the use of biocides should not relinquish the need for care being taken to ensure minimal microbial activity or periodic monitoring. If biocides are desired for use, products such as Kill-Em™ or GrotaMar 71® are commercially available for purchase and use.

2.8 Summary

Irrigation applied to agronomic crops during the growing season has shown positive implications in terms of increasing yield. For oilseed crop production, increased yields result in amplified oil availability, thereby enhancing biodiesel output potential. However, oilseed constituents important for a small-scale, on-farm biodiesel production system include oil content along with FFA and protein. Low FFA is desired for least expense in ester conversion from the vegetable oil and high protein content is advantageous for livestock feed ration supplementation. Oilseed cake, which will contain the majority of the protein in the oilseed, can be utilized to offset livestock feed costs and contribute to the economics of an on-farm biodiesel production system. These constituents have shown no significant responses to irrigation if sufficient rainfall was received during the growing season of the respective crop. The actual composition of oilseeds depends on many factors, including genotype, growing season, geographic location, and agronomic practices (Boydak et al., 2002 and Bellaloui and Mengistu, 2008). Also, some research suggested that increased water quantity, not irrigation interval, may negatively impact oil

concentration in soybeans (Sprecht et al., 2001) while protein concentration was inversely correlated to oil content (Specht et al., 2001).

Irrigation alone may not necessarily be the deciding factor in oilseed constituents. Other parameters such as macronutrients and even micronutrients had an impact on oil content, protein concentration and yield within canola and cottonseeds (Sims et al., 1993, Sprecht et al., 2001 and Sawan et al., 2006). Sawan et al. (2006) also found that FFA could be decreased in cottonseed with applications of macronutrients. Environmental factors other than those imposed by irrigation or nutrients can also impact oilseeds. Damage by heat, wet weather, excessive moisture, poor storage, or other unfavorable conditions required extensive processing to obtain an edible or usable product plus have poor stability during storage.

Hydrolysis is another factor that can heavily impact feedstock and biodiesel quality. Andersson and Lingnert (1998) found that metal traces such as copper or iron enhance hydrolysis. These metals can come in contact with oil or biodiesel in mechanical screw presses or storage containers. Seeds, oil and biodiesel are all susceptible to hydrolysis with degree of unsaturation influencing hydrolysis stability (Merrill et al., 2008). However, measures can be taken to prevent degradation. Seeds should be stored in cool dry places while oil and biodiesel should be stored in dry, airtight containers not in direct sunlight or exposed to elevated temperatures.

There are several methods used in the transesterification process with different concentrations of catalysts or alcohols. Acceptable reactions can occur at different temperatures and time durations. However, base catalyzed transesterification proved to be the most effective and least expensive from chemical cost as well as time requirement. Research suggested that one wt.% NaOH, 6:1 molar ratio of alcohol to oil, reaction temperature of 60 ^{o}C and reaction time of one hour is sufficient to satisfactorily transesterify vegetable oils with less than 0.5% water and less than 2% FFA. Feedstocks with higher

water or FFA contents will require further processing or pretreatment before transesterification to obtain a quality product.

Care should be taken when storing biodiesel long-term to ensure water does not contaminate a storage tank. Frequent monitoring of a storage tank as well as periodic draining of free water from the bottom of a tank can ensure an environment conducive for microbial activity is not present. Water can enter storage tanks from vents or seals in the storage tank. Biodiesel is hydrophilic and hygroscopic and can absorb moisture and water. Additionally, high storage temperatures of approximately 40 ^{o}C can degrade biodiesel especially when biodiesel is exposed to air. Biodiesel degradation or oxidation can yield a carbon source from which bacteria may propagate. While biodiesel degradation may promote timely remediation of soil or water in the event of a spill as compared to petroleum diesel, there are negative connotations associated with long-term storage stability of biodiesel. If bacterial growth is not prevalent in an existing storage tank, biocides may be used for control measures.

Small-scale, on-farm systems are proved to be marginally feasible in Oklahoma. Kenkel and Holcomb (2006) concluded that on-farm biodiesel production was not feasible at commodity prices experienced after 2005. Returns were sensitive to the farm level price of commodities, biodiesel, and meal value. On-farm processing of oilseed higher in oil content (canola, sunflower) was marginally feasible, but feasibility of soybean based biodiesel required a biodiesel value above $1.32/liter with historically high meal prices.

CHAPTER THREE
RESEARCH METHODS

3.1 Introduction

This chapter outlines methodologies used within this study to attain the three research objectives. First, those for the experimental irrigation energy crop rotation will be presented, followed by methodology used in determining best-practices for conversion of vegetable oils into biodiesel, phosphorus removal from vegetable oils, and vegetable oil storage procedures conducive to a small-scale, on-farm biodiesel production. Methanol recovery assessment and biodiesel quality of an in-house processor will then be discussed followed by biodiesel quality of degummed oils. Also included will be procedures used to assess the efficiencies of in-house mechanical extruders with varying oilseeds. Lastly, methodology for an economic assessment of a current small-scale biodiesel production system and proposed small-scale, on-farm biodiesel production operation will be outlined. Included are variables tested along with statistical analyses performed.

3.2 Irrigation Experiment for a Non-traditional Energy Crop Rotation

A split-plot experimental design consisting of 48 plots was used for this experiment at the Tennessee Valley Research and Extension Center, Belle Mina, Alabama (Figure 3.1). Each plot was 12.2 m in length by 11.9 m in width with the middle two rows or 1.5 m harvested for yield and other experimental data. The plots consisted of two rotations with a crop growing regimen of 1) continuous cotton and 2) canola-soybeans-cotton grown with six different irrigation treatments. Irrigation

treatments included rainfed, 25%, 50%, 75%, 100% and 125% pan evaporation replenishment levels adjusted for crop canopy. All cotton plots were planted around the third week of April with irrigation commencing in June depending upon cotton vegetative growth and environmental conditions. Soybeans were planted the third week of June for the canola-soybeans-cotton plots followed by cotton planted in the third week of April of the following year. After the fall cotton harvest from the canola-soybeans-cotton plots, in the first part of October, canola was planted and then harvested the following second week of June. The experiment commenced in October, 2007 with the planting of canola and concluded in October, 2010 with the harvesting of cotton from rotation 1 and soybeans from rotation 2. The study site was under no-tillage management with soil fertility directed according to Alabama Cooperative Extension System fertility recommendations. Soil samples were collected within each plot after each fall harvest at a depth of 0 – 15 cm. Samples were analyzed for fertility and pH levels by the Auburn University Soil Testing Laboratory, Auburn, Alabama.

An irrigation scheduling spreadsheet was developed to closely monitor pan evaporation and crop canopy cover with the information used to determine daily application levels for each plot. Pan evaporation was determined from AWIS Weather Services, Inc. (www.awis.com) and daily rainfall was recorded with both parameters entered into an MS Excel spreadsheet on a daily basis. Crop canopy was measured weekly and a percentage value assigned relative to soil area covered between rows. Canopy cover was also recorded in the MS Excel spreadsheet. These parameters were used to calculate an application run-time for the irrigation system (eqn. 1). Water was applied to all plots at a rate of 2.26 cm/hr with irrigation commencing when the accumulated pan evaporation, adjusted for canopy cover, required a minimum of 21 minutes of application for replenishment. In order to determine when the 21 minute threshold was met, daily calculated irrigation run-time was carried over and added to the next day until a minimum of 21 minutes was reached. Run-times for a treatment were then programmed into

a Rain Bird© Maxicom^2 Central Control (Rain Bird Corporation, Azusa, CA) irrigation controller when required.

A combine with a platform header width of 1.52 m was used to harvest soybeans corresponding to a harvested area of 18.6 m^2. The center pass was harvested for data analysis with the accumulated weight determined using a weigh buggy. Another combine with header width of 1.1-m was used to harvest canola making two passes across the plot center for data analysis with the approximate area harvested being 27 m^2 and yield was calculated after cleaning the seeds to remove trash. Canola was grown at 18-cm row spacing with the 12 center rows (2.2-m) harvested for data analysis. Cotton was harvested using a 2-row cotton picker with the center 4 plot rows used for yield data with seed cotton yield computed by dividing the harvested, accumulated mass by the harvested area. All yield calculations were the same for all crops.

$$Runtime = \frac{Pan \times CC \times TRT}{AR} \times 60 \tag{3.1}$$

where,

Runtime = irrigation runtime (min.)
Pan = AWIS pan evaporation (cm)
CC = percent canopy cover (%)
TRT = irrigation treatment (%)
AR = irrigation application rate (cm/hr)

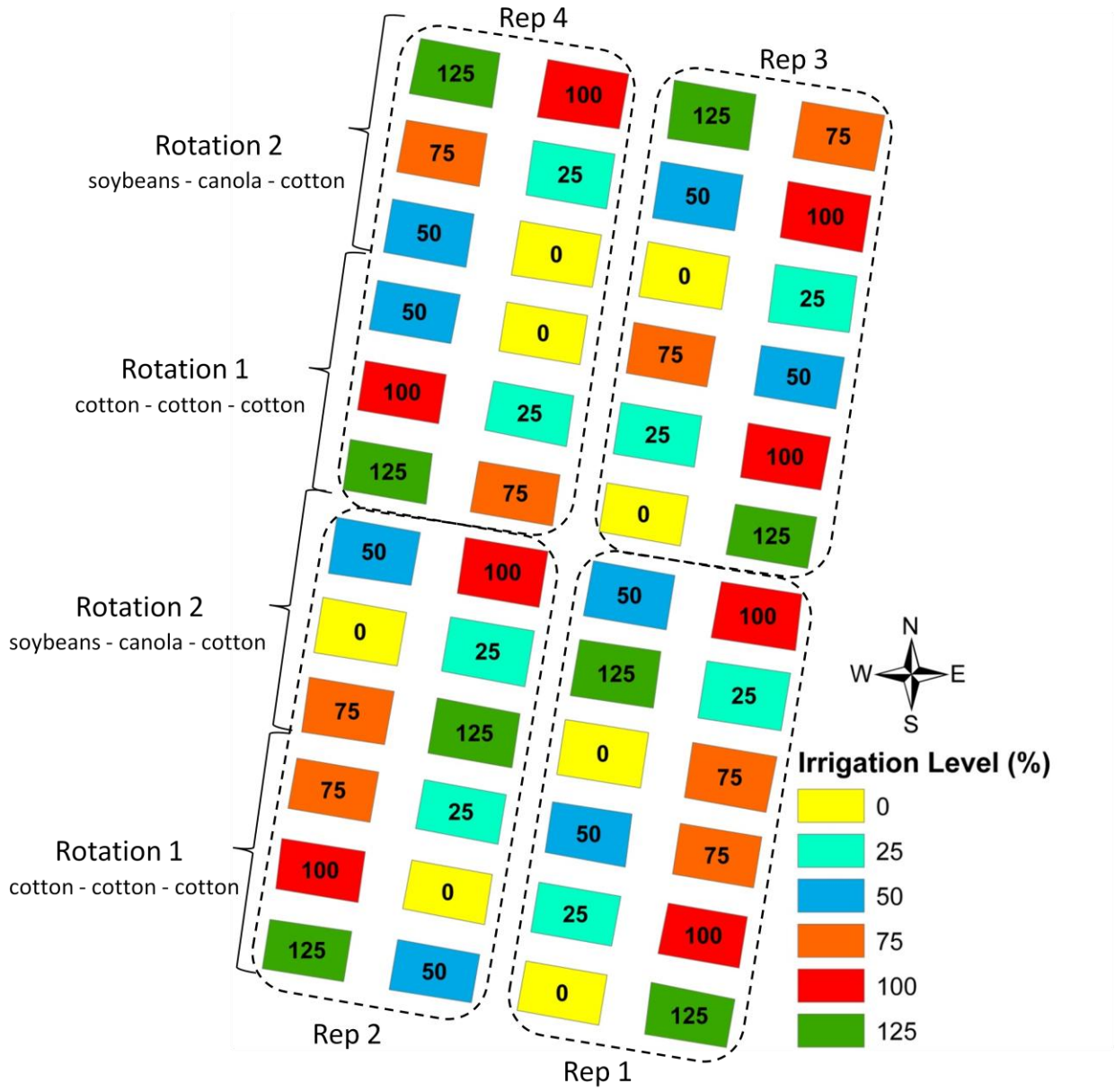

Figure 3.1. Layout of study site and treatment assignment.

Fifty cotton boll samples were handpicked from the cotton plots just prior to harvest. The cotton samples were ginned using a laboratory scale, 10 saw cotton gin with the seeds being chemically de-linted. Immediately after harvest, canola and soybean seed samples were analyzed for moisture content using a Dickey John GAC 2100b moisture meter, however, cottonseed sample moisture contents were measured at the time of seed analysis. All samples were analyzed by Hahn Laboratories, Columbia, SC.

De-linted cottonseed composite samples by plot were analyzed for protein (AOCS Official Method, 2009b), oil (AOCS Official Method, 2009a), and FFA (AOCS Official Method, 2009c). Canola composite samples by plot were analyzed for protein (AOCS Official Method, 2009h), oil (AOCS Official Method, 2009g), and FFA (AOCS Official Method, 2009f). Soybean composite samples by plot were analyzed for protein (AOCS Official Method, 2009e), oil (AOCS Official Method, 2009d), and FFA (AOCS Official Method, 2009f).

3.3 Review of Biodiesel Production Procedures

To evaluate the quality of biodiesel to be produced in a small-scale on-farm setting, a biodiesel production procedure must first be determined that yields satisfactory fuel at low input costs. The first step in the process was to conduct a literature review of biodiesel production procedures. Research of biodiesel production procedures using varying chemicals, procedures and feedstocks is well documented and further experimentation of multiple procedures is unnecessary. Therefore, this literature review consisted of recording procedure and result information including: catalyst type and amount used, alcohol type and molar ratio with respect to oil, reaction time and temperature and conversion efficiency. Because ASTM Standard D 6751 (2007) requires a transesterification conversion efficiency of 98% for the retail of biodiesel, the literature review focused on transesterification conversion efficiencies near or exceeding this value. However, in order to assimilate a comprehensive list, biodiesel production procedures yielding 95% transesterification conversion efficiency or greater were included as a potential recommended production procedure. The production procedures that did meet the conversion requirement to be included were evaluated first by chemical amount required and second on reaction time and ranked accordingly. These two parameters were assumed to be of most importance to a farmer. The method of least expense and reaction time was then used to produce biodiesel for experiments outlined below.

3.4 Vegetable Oil Storage Experiment

3.4.1 Triglyceride Hydrolysis

Since FFA concentration heavily dictates simplicity of biodiesel production, it was recommended that oil with concentrations less than 2% be used as biodiesel feedstocks for base catalyzed transesterification methods. Oil stored in conditions exposed to the atmosphere and subject to heat, can lead to hydrolysis and increased FFA concentration. Therefore, tests were performed to assess FFA concentration changes under sealed container storage conditions on WVO, cold pressed canola oil, and cold pressed soybean oil. Assuming oil will be stored on-farm and pre-phosphorus removal, only crude oil samples were stored in this experiment. Oil storage simulated typical on-farm techniques that would be used by a farmer. During the pressing of the oilseeds (e.g. canola and soybeans), four random one-gallon samples of each oil type were collected starting at 30 minutes after press warm-up and continuing at one-hour intervals afterward until all samples were collected. These samples were placed in sealed, one-gallon HDPE (high density polyethylene) containers.

Figure 3.2. Vegetable oil storage experiment.

Water in vegetable oil can expedite triglyceride hydrolysis and FFA accumulation and was initially tested in each sample prior to beginning the experiment. After soybean and canola oils had been mechanically extruded and WVO had been collected from Auburn University dining facilities, each replicate sample was tested using ASTM Standard E 203-01 (2001). All samples were stored in a non-climate controlled room to simulate oil storage in an on-farm shed or barn (12 samples total including four random samples of WVO collected from AU dining facilities). Figure 3.2 shows the samples used for this experiment. One-liter amber glass bottles were used for auto-claved control samples (WVO and canola, respectively) and to prevent hydrolysis due to sunlight. Four-liter containers were used to store samples of canola, WVO and soybean oils respectively. A summary of replications are as follows:

- WVO
- Cold pressed canola oil
- Cold pressed soybean oil
- Cold pressed auto-claved canola oil control
- Auto-claved WVO control

Samples were tested monthly for FFA concentration according to ASTM Standard D5555-95 (2008) to determine rate of hydrolysis and for OD (optical density) to determine if microbial growth was present. The duration of the experiment was approximately nine months. Prior to FFA testing, each sample was shaken vigorously for 20 seconds in the sealed storage container to homogenize the sample and avoid stratification. Temperature measurements were recorded every 30 minutes during the duration of the experiment using Dickson SM 325 display temperature data loggers (Dickson, Addison, IL) (Figure 3.2) to understand the relationship of temperature to oil hydrolysis. Two thermocouples were suspended beside the storage containers and two were placed inside containers of oil. All containers were sealed from the atmosphere.

3.4.2 Microbial Contamination

Microbial growth may only be present if a free water layer exists because water bound in the fuel or oil is unusable for microbial growth. Therefore an experiment was performed, in conjunction

with the triglyceride hydrolysis research (Section 3.4.1), to determine if moisture in the seed or moisture accumulated over the storage period was sufficient to lead to microbial growth. The design and experimental procedures were the same as Section 3.4.1. However, control samples were included in the event microbial contamination existed in the samples prior to storage. Four control samples of canola oil, 0.5-L each, were collected concurrently with mechanically pressed experimental samples and four 0.5- L WVO control samples were collected from AU dining facilities. Control samples were stored in amber glass containers and autoclaved to reduce hydrolysis due to light exposure and sterilize the feedstock, respectively. They were then stored in the same location and conditions of the non-control samples (Figure 3.2).

Once per month for approximately nine months, samples were tested for microbial contamination. All samples were vigorously shaken initially for 20 seconds to homogenize the oil in the event any stratification had occurred during storage. A 100-µl sample was drawn from each of the non-control sample containers and placed in a clear bottom, 96 well microplate. Control samples were only opened inside a Labconco© Purifier Biological Safety Cabinet (Labconco Corporation, Kansas City, MO). The bio-safety cabinet was cleaned with ethanol and sterilized with 5 minutes of exposure to an ultra-violet light. The amber glass bottles containing the oil were placed inside the cabinet then opened to collect a 100-µl sample which was added to the tray. Four 100-µl samples of distilled water were also added to four wells in the tray for control measurements. Next, the microplate was placed in a Spectramax M2 Microplate Reader (Molecular Devices, Sunnyvale, CA) ultra-violet spectrophotometer. The samples were tested for absorbance at a spectral range of 420 to 650 nm with an incremental step of two nanometers. Bacteria typically have an absorbance of 550 nm, so this wavelength will be the focus of the results.

To ascertain results, bacteria positive samples in the ultra-violet spectrophotometer, bacteria positive control samples were created using *Pseudomonas putida* and either water or WVO. Five

bacteria concentrations were selected to test. *Pseudomonas putida* was cultured in substrate and volumetric samples of 1 ml, 2 ml, 5 ml, and 10 ml were measured from the culture and centrifuged to separate the bacteria and substrate. The bacteria samples were then washed twice with the respective media it was to be tested in (water or WVO) to remove traces of the culture media. To wash the bacteria, the culture media was poured off after centrifugation, then 2 ml of the media (water or WVO) were added to the vial, the vial was then vortexed to mix the bacteria and media. Next, the mixture was centrifuged and the process was repeated once more. After washing, 100 µl of media was added to the bacteria and the sample was vortexed again to thoroughly mix the bacteria and media. Then a 100-µl positive control sample was drawn from the vial and placed in the 96 well microplate for absorbance analysis. A control sample of each media was measured for absorbance as well. *Pseudomonas putida* was used as the bacteria in the positive control samples because it was readily available and its absorbance value at a 550-nm wavelength is similar to other bacteria that might grow in vegetable oil storage containers.

3.5 Methanol Recovery Efficiency Experiment

The transesterification reaction is pushed to completion with the addition of approximately twice the amount of methanol required and excess must be removed after the reaction for safety and efficiency reasons. The current methanol recovery process of the Biodiesel Logic processor (Biodiesel Logic, Inc. Troy, AL), located in Auburn University's Biosystems Engineering department, was believed to be poor and the addition of a vacuum pump may increase methanol recovery efficiencies. For this reactor, the current alcohol recovery process will be assessed for efficiency by analyzing biodiesel pre- and post-alcohol recovery using an evaporative method of methanol determination. The implementation of a vacuum pump for alcohol recovery will be assessed in the same manner. Current transesterification methods performed with this processor by lab technicians entail a volumetric ratio of

5:1 oil to methanol or approximately 4.79:1 molar ratio of methanol to oil. Since the chemical reaction requires 3:1 molar ratio of methanol to oil, 1.79 moles of methanol per mole of oil can be recovered or distilled from the biodiesel/methanol mixture. For a 90-L batch of oil, this amount equates to approximately 6.69 L of methanol.

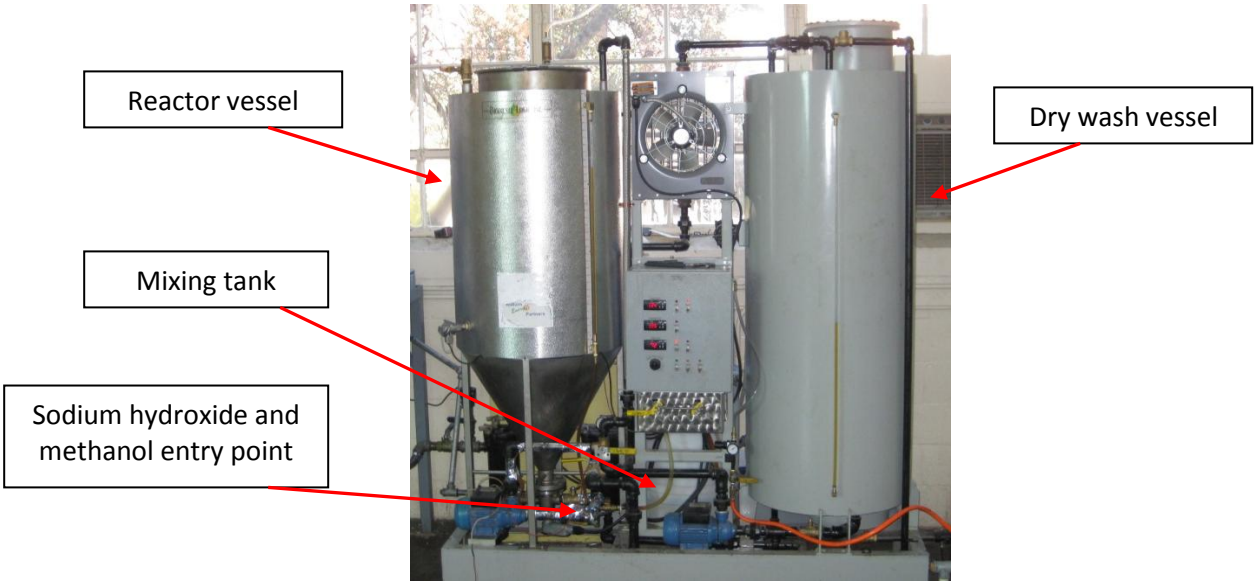

Figure 3.3. Biodiesel Logic Processor (Biodiesel Logic, Inc. Troy, AL).

The maximum batch capacity of the Biodiesel Logic biodiesel processor is 208-L, however, 90-L batches were processed in this experiment to ensure WVO consistency and storage reserves were not depleted. Once 90-L of WVO were added to the reactor vessel (figure 3.3), the oil was heated to 57 ^{o}C. Upon the WVO reaching the desired temperature, chemical grade methanol (17.9-L) and sodium hydroxide (NaOH), granular form, were mixed for three minutes in the small HDPE (high density polyethylene) chemical mixing tank of the reactor. The amount of sodium hydroxide added was dictated by the FFA% of the oil. A 1-ml sample of oil from each batch was titrated using ASTM Standard D 5555-95 (2008) to determine FFA% as oleic. The sodium hydroxide and methanol mixture was pneumatically pumped into the reactor while the WVO was being circulated in the reactor vessel. The mixture entered the reactor through the oil circulating pipeline just in front of the pump and was vigorously mixed with

the oil as both were pumped to the top of the reactor and discharged into the vessel. This form of mixing is the only active mixing that took place during the reaction; therefore, the reaction time was increased from manufacturer recommendations of one hour to three hours. Upon completion of mixing for the reaction, the mixture was allowed to cool and glycerol was allowed to gravitationally settle from the biodiesel. The mixture cooled to at least 41 ^{o}C before glycerol was drained off through a valve in the bottom of the reactor vessel.

After the glycerol was drained, the biodiesel underwent methanol recovery by one of the treatments outlined below. The biodiesel was heated to 80 ^{o}C in order to vaporize the residual methanol not consumed in the reaction. A small tube in the top of the reactor vessel allowed vapors to travel to a condenser. The condenser consisted of a water jacket or double walled tube in which chilled water was pumped through with a commercially available 12-volt water pump. The chilled water was kept at or near 0 ^{o}C at all times. During methanol recovery, a valve at the outlet of the condenser tube was opened and condensed methanol was collected in a vessel. For the standard methanol recovery process outlined by the manufacturer (standard), methanol vapor was thought to have entered the condenser only because of vapor pressure in the reactor. However, the vacuum treatment consisted of methanol recovery with the assistance of a Gast Manfacturing, Inc vacuum pump model DOA-P704-AA (Gast Manufacturing, Inc., Benton Harbor, MI). The vacuum pump line was plumbed into the methanol catchment vessel and created 129 mm Hg negative pressure in the system. Along with slightly lowering the boiling point of methanol, the methanol vapors were allowed to more freely move towards the condenser. Methanol recovery was allowed to run for 4 hours, as recommended by the manufacturer.

A randomized complete block experiment was designed to test methanol recovery efficiencies as a result of each treatment. Four replications were performed. Each replication consisted of two treatments that were randomly assigned, either vacuum pump assisted (vacuum) or standard methanol recovery procedure (standard). Random 50-g sample from each batch of biodiesel produced were

collected after methanol recovery and for efficiency analysis purposes. The samples collected are outlined in table 3.1 and were “BD post methanol recovery” and “glycerol”.

An evaporation method was used for methanol determination in biodiesel samples post methanol recovery and glycerol samples. This analysis resulted in a volumetric methanol balance of the system. A known volume of methanol was initially added to the WVO; part of it was consumed in the transesterification reaction and can be determined using equation 3.2 and assuming three moles of methanol are consumed in the transesterification reaction for every one mole of WVO. A portion of methanol was recovered using the experimental procedures above and was volumetrically measured after methanol recovery concluded. A portion of methanol separated from the biodiesel with the glycerol layer and was drained from the reactor. Another portion of the methanol was residual in the biodiesel. The residual methanol content in glycerol and biodiesel was measured using the evaporative method.

A Rotavapor R110 (Büchi Laboratory Equipment, Switzerland) was used to evaporate methanol from all samples. The water bath was heated to only 70 ^{o}C to avoid volatilizing non-methanol portions of the sample. Approximately 50 g of sample was placed in the round bottom flask and weighed. The flask was attached to the rotary evaporator, chilled water was passed through the condenser during the experiment, and the vacuum pump was attached to the rotary evaporator operating at a negative pressure of 129 mm Hg. Each sample was allowed to evaporate for 1.5 hours. The round bottom flask and its contents were then weighed and the final weight was recorded. To ensure the integrity of this method and prior to the actual experiment, control samples of a mixture of purified canola oil and a known amount of methanol were evaporated under the conditions outlined above.

$$M = \frac{C * V * \rho_O * 3 * MW_M}{MW_O * 10 * \rho_M} \quad (3.2)$$

where,

M = Methanol consumed during transesterification (L)
C = Conversion efficiency of transesterification (%)
V = Volume of oil transesterified (L)
ρ_O = Density of oil (kg/L)
MW_M = Molecular weight of methanol (g/mol)
MW_O = Molecular weight of oil (g/mol)
ρ_M = Density of methanol (kg/L)

Table 3.1. Methanol recovery experiment summary.

TRT	Vacuum	Standard
Samples collected	Raw BD	Raw BD
	BD post MeOH recovery	BD post MeOH recovery
	BD post dry wash	BD post dry wash
	WVO	WVO
	glycerol	glycerol

BD denotes biodiesel
Post MeOH recovery denotes after methanol recovery from raw biodiesel
Post dry wash denotes after washing biodiesel with AMBERLITE™ BD10DRY resin for purification

3.6 Phosphorus Removal from Vegetable Oil Experiment

Simple, cost effective methods of degumming vegetable oils were explored in this Section that required non-hazardous chemicals and simple procedures. Further, gravitational separation of oil and gums was utilized for these experiments, where applicable, to obtain results a typical farmer may experience.

3.6.1 Hot Water Method

A hot water method of phosphorus removal was adapted from Brekke (1980). He stated that hydration by the addition of water causes most phosphatides (phospholipids) and gums present in a crude oil to become insoluble in the oil. The phosphatides, proteins, and other colloidal impurities are hydrated by the hot water and swell or expand forming gels of higher specific gravity than the vegetable oil and agglomerate as flocculent particles, which can be gravitationally separated (figure 3.4). Three, 150-ml samples of each crude oil type (soybean and canola) were placed in erlenmeyer flasks and

heated in a New Brunswick Scientific, Innova 40 incubator shaker (Edison, NJ) (figure 3.2) to 65 ^{o}C. Once heated, the samples were mixed with water, based on the average phosphatide content for the respective oil, and mechanically agitated at 200 rpm for 30 minutes. Brekke (1980) stated that the appropriate amount of water to add was equivalent to 75% of the phosphatide content in the oil. Soybean oil can contain 1.1 to 3.2 vol.% phosphatides, with the average being about 1.8 vol.%, therefore 2.1 ml (1.4 vol.%) of water was added. Canola oil contains on average 1.25% phosphatide (Przybylski, 2001), therefore 1.4 ml (0.94 vol.%) of water was added to canola oil samples. Once the samples were agitated for 30 minutes, they were allowed to cool and settle for two days according to procedures outlined by Brekke(1980). Hot water degummed oil samples were analyzed by Hahn Laboratories, Columbia, SC and AOCS Official Method (2009j) was used to determine phosphorus concentrations.

3.6.2 Citric Acid Method

The citric acid phosphorus removal procedure used in this experiment was adapted from Diosady (1982). Three, (150 ml) samples of each oil type (soybean and canola) were placed in erlenmeyer flasks and heated to 65 ^{O}C in a New Brunswick Scientific, Innova 40 incubator shaker (Edison, NJ) (figure 3.2). A 50% aqueous citric acid solution was added to the oil until a concentration of 2,500 mg/kg citric acid to oil was obtained (675 g of citric acid solution). After the oil was mixed for 10 minutes at 200 rpm, a further aliquot of 2 wt% water was added for hydration. Agitation continued for 20 minutes, then the oil was allowed to cool and gums settled from the oil for two days. The citric acid removed non-hydratable phospholipids and the water removed hydratable phospholipids. When the mixture cooled, a phase separation appeared in which the degummed oil was on top and the water and phospholipids on the bottom (figure 3.4). The degummed oil was then decanted. Citric acid degummed oil samples were analyzed by Hahn Laboratories, Columbia, SC and AOCS Official Method (2009j) was used to determine phosphorus concentrations.

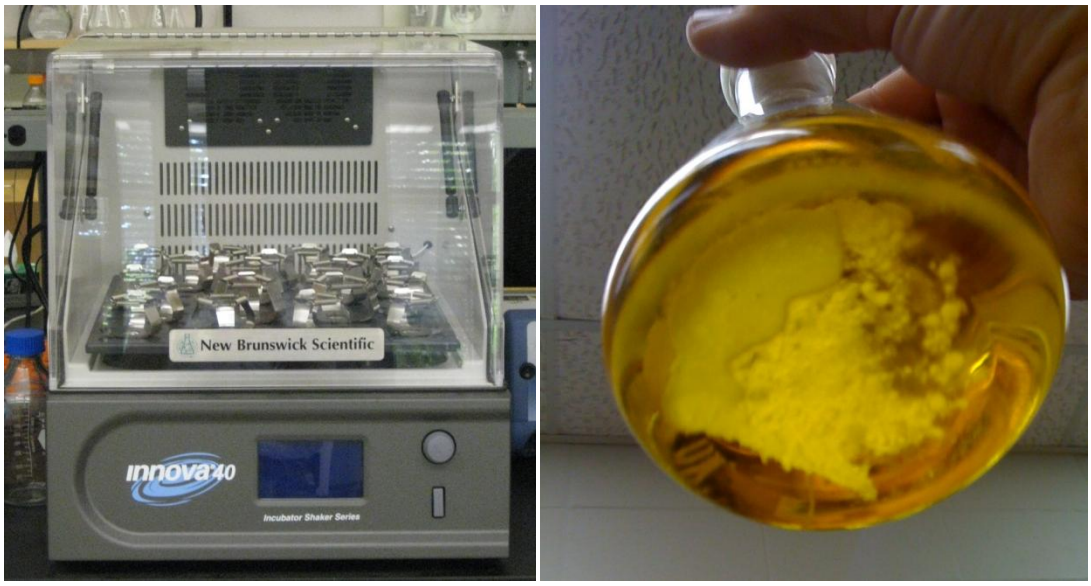

Figure 3.4. Incubator shaker used for agitation of oils (left) and settled gum phase in soybean oil (right).

3.6.3 Anion Exchange Resin Method –AMBERSEP™ BD19

AMBERSEP™ BD19 was used as a third method of phosphorus removal. Procedures for this experiment were followed according to manufacturer's recommendations (The Dow Chemical Company, Midland, MI) and were confidential. A Nexus 6000 Ultra High Pressure syringe pump by Chemyx Inc., Stafford, TX (figure 3.5) was used to meter fluids into the column at a controlled rate. First, five volumes of dry methanol were injected into the reactor using the syringe pump, displacing the water used for setup. Before experimental samples were collected, 200 ml of soybean oil were metered through the column to remove methanol. A resin depletion test was required, so 100 ml of soybean oil was then put through the column to document initial resin effectiveness in removing phosphorus.

Next, 600 ml of soybean oil was put through the column, three 100-ml samples for phosphorus analysis and three 100-ml samples for transesterification. Then, 200 ml of canola oil was pumped through the column to avoid cross contamination in experimental canola samples. A volume of 600 ml

Figure 3.5. Column positioned inside oven (left), oil preheating on the hotplate (center), and syringe pump metering oil into the column through the top of the oven (right).

of canola oil was then put through the column, three 100-ml samples for phosphorus analysis and three 100-ml samples for transesterification. To ensure no cross contamination, 200 ml of soybean oil was metered through the column, then 100 ml of soybean oil was pumped through the column to complete the depletion test sampling. Table 3.2 summarizes complete throughput of oil into the column. AMBERSEP™ BD19 degummed oil samples were analyzed by Hahn Laboratories, Columbia, SC and AOCS Official Method (2009j) was used to determine phosphorus concentrations.

Table 3.2. Order of operations for AMBERSEP™ BD19 phosphorus removal experiment.

Order	Operation
1	Inject 200 ml of soybean oil to remove methanol
2	Inject 100 ml of soybean oil for resin depletion test
3	Inject 600 ml of soybean oil (three 100 ml samples for phosphorus analysis, and three 100-ml samples for transesterification)
4	Inject 200 ml of canola oil to avoid contamination
5	Inject 600 ml canola oil (three 100 ml samples for phosphorus analysis, and three 100-ml samples for transesterification)
6	Inject 200 ml of soybean oil to avoid cross contamination
7	Inject 100 ml of soybean oil to complete depletion test

3.6.4 Control

Three control samples of both oil types (soybean and canola), having no phosphorus removed, were analyzed for phosphorus concentration in order to determine effectiveness of each degumming method outlined above. Control samples were analyzed by Hahn Laboratories, Columbia, SC and AOCS Official Method (2009j) was used to determine phosphorus concentrations.

3.6.5 Experimental Design

A randomized, complete block experimental design was developed to test feasibility and effectiveness in phosphorus removal according to the procedures outlined above. Using an in-house mechanical screw press, canola harvested from Tennessee Valley Research and Extension Center (Belle Mina, AL), was pressed and at three random times during pressing, oil samples were drawn from the press signifying three replications. Each replication was further split into four samples. Each of the four oil samples were randomly assigned a method of phosphorus removal (i.e. hot water, citric acid, or AMBERSEP BD19 ion exchange resin) or control. The same experimental design was implemented for soybean oil as well. Eight tests with three replications each were performed for a total of 24 tests. A summary of test replications is illustrated in table 3.3.

Table 3.3. Summary of phosphorus removal tests performed.

Oil Type	Phosphorus Removal Treatment
Soybean	Hot water
	Citric Acid
	AMBERSEP™ BD19 resin
	Control
Canola	Hot water
	Citric Acid
	AMBERSEP™ BD19 resin
	Control

3.7 Biodiesel Quality Experiment

3.7.1 Biodiesel Logic, Inc. Biodiesel Processor

In conjunction with the methanol recovery experiment performed on the Biodiesel Logic biodiesel processor, a concurrent experiment was performed to assess biodiesel quality. Given the fact that raw biodiesel is heated and agitated again during methanol recovery and that it is washed in a dry wash procedure using AMBERLITE™ BD10DRY (Rohm and Haas Company, Philadelphia, PA), two objectives were sought from this experiment. The first was to determine if post reaction or transesterification during methanol recovery occurred. Glycerol release during methanol recovery is an indication that insufficient mixing occurs during transesterification in the reactor vessel. Inadequate reaction could be due to the fact that the only agitation of the WVO, sodium hydroxide and methanol mixture was in the pump as previously discussed; however, increasing the reaction time from one hour to three hours may have nullified insufficient agitation. The second objective of this experiment was to determine the dry wash resin's efficiency in removing free glycerin from biodiesel. AMBERLITE™ BD10DRY was advertised by the manufacturer to remove, among other things, free glycerin. Analysis of biodiesel pre- and post-washing could determine if this resin removed free glycerin from the biodiesel.

In addition to transesterification steps mentioned in Section 3.5 using the Biodiesel Logic biodiesel processor and after methanol recovery was performed, biodiesel was transferred to the dry wash vessel (figure 3.5). Once the temperature of the biodiesel was <38 ^{o}C the dry wash procedure was performed. The manufacturer recommended optimal washing temperature below 38 ^{o}C and an integrated thermocouple prevents washing at temperatures exceeding 38 ^{o}C. A column inside the washing tank of the Biodiesel Logic biodiesel processor held approximately 18 kg of AMBERLITE™ BD10DRY. Biodiesel was pumped from the dry wash vessel into the top of the column containing the resin with maximum outlet pressure into the column of 155 mm Hg with the process performed over

four hours. A 50-g sample of biodiesel post dry wash from each replication was collected for quality analysis. Upon completion, the biodiesel is said to be a "finished product" and pumped from the processor into a storage vessel for future use. The exact experimental design used in Section 3.5 was used for quality assessment. Samples collected for this analysis are outlined in table 3.1 and were "raw BD", "BD post MeOH recovery" and "BD post dry wash."

3.7.2 Degummed Oils

Degummed oil samples from Section 3.6 outlined above were transesterified to determine quality of biodiesel produced as a result of the specific degumming method. The transesterification procedure was determined from published literature and frequently used by researchers. Methanol was used as the alcohol and sodium hydroxide (NaOH) as the catalyst for transesterification. Procedures were based on the work of Freedman et al. (1984a). Chemical concentrations, reaction time and temperature are outlined below.

- Molar ratio of methanol to oil of 6:1
- One wt.% NaOH
- 60 ^{o}C reaction temperature
- One-hour reaction time

Approximately 95 g of each oil sample was placed in an erlenmeyer flask and capped with a rubber stopper. The samples were placed in a New Brunswick Scientific, Innova 40 incubator shaker (Edison, NJ) and agitated at 100 rpms until the desired temperature of 60 ^{o}C was reached. In the meantime, a sodium hydroxide and methanol mixture was produced. The mixture was then added to the heated oil and the mixture was agitated at 200 rpm for one hour, maintaining a temperature of 60 ^{o}C. After the reaction, the biodiesel/glycerin mixture was allowed to cool to room temperature and gravitationally settle overnight before decanting. The glycerol released by the reaction was removed.

Like the samples above, a GC was used to analyze these samples as well with conversion efficiency being calculated. As a secondary analysis, samples will be analyzed for phosphorus as

transesterification has the potential to remove a portion of the phospholipids. Three replicates of each oil type/degumming method combination were transesterified and are outlined in table 3.3 with the exception of three replicates of WVO added as a control and for comparison purposes.

Biodiesel samples from the above two experiments were analyzed using a gas chromatograph (GC) with a modified method designed by an Auburn University Biosystems Engineering post doctoral fellow to measure free glycerin, monoglyceride, diglyceride, and triglyceride in biodiesel. Thus, allowing for calculation of conversion efficiency, weight percentage of free glycerin and weight percentage of total glycerin. The latter two are requirements of ASTM Standard D6751 (2007) and must be <0.02 wt% and <0.24 wt%, respectively to adhere to the standard.

To determine concentrations of free glycerin and total glycerin in the experimental biodiesel samples, 0.1 g of each sample were measured using a RADWAG WAX 110 (North Miami Beach, FL) balance that records to the ten-thousandths decimal place and placed in a 10-ml glass vial with a sealable cap. A volume of 100-µl of each standard solution, (S) – (-) – 1,2,4-Butanetriol (Internal Standard 1), 1,2,3-Tridecanolyglycerol (Internal Standard 2) and N-methyl-N-trimethylsilyltri-fluoracetamide (MSTFA), was added to the biodiesel sample, respectively. The solution was allowed to sit for 15 minutes while the MSTFA digested the biodiesel sample. Next, approximately 8 ml of heptanes were added to the mixture and sub-samples were placed into GC vials for testing. An Agilent Technologies gas chromatograph model 7890A (Agilent Technologies, Santa Clara, CA) The GC method used was ASTM Standard D 6854-00 (2006) with the exception of a split/splitless inlet in splitless mode at a temperature of 320 ^{o}C. To ensure water content in WVO did not affect or inhibit transesterification, a volumetric Karl Fischer titration was performed on all samples. ASTM Standard E 203-01 (2001) was adhered to for water analysis.

3.8 Mechanical Extruder Efficiency Analysis

A wide array of mechanical screw presses, designed to extrude vegetable oil from oilseeds, are commercially available. Some cold press extruders require specialized skill to optimize oil output, while others demand minimal operator input as most parts are in fixed positions. Currently, there are two different mechanical oilseed presses housed in Auburn University's Biosystems Engineering biodiesel laboratory. The Henan Double Elephant Machinery Co., Ltd (Henan, China) model 6YL-120 and Karl Strähle GmbH & Co. KG (Dettingen, Germany) SK 60/2 presses are rated, by the manufacturer, at capacities of 6 tonnes and 720 kg of seed throughput per 24-hour period, respectively. To evaluate the capacity and primarily compare oil extraction efficiencies, tests were conducted with canola near optimal moisture content for oil extraction, 6.5%wb for canola. Soybean and sunflower were also assessed on the Henan Double Elephant Machinery Co., Ltd model 6YL-120. A known mass of oilseed was extruded in the mechanical screw presses with three replications completed. From these tests, the following mean data was calculated and used to evaluate press performance:

- Average oilseed processed (kg/hr)
- Average volume of oil produced (L/hr)
- Average mass of oilseeds in versus volume of oil out (kg/L)
- Extraction efficiency (oil out/theoretical oil available, %)

3.9 Economic Analysis of Small-Scale Biodiesel Production Systems

3.9.1 Auburn University's Biosystems Engineering Biodiesel Production System

Currently, in Auburn University's Biosystems Engineering Department, an ongoing project exists in which staff employees collect WVO from the three dining facilities on Auburn's main campus and process this oil into biodiesel. This system closely parallels one that might exist on-farm and actual economics are valuable in assessing the feasibility of an on-farm biodiesel production system.

The system consisted of a part-time staff member who collects WVO from campus locations and processes biodiesel. At each dining facility, several 30-gallon drums are placed on spill pallets and dining facility staff empty used oil into the barrels. Spill pallets and 30-gallon drums (figure 3.6) are required by Auburn's Risk Management division which may not be used for an on-farm process.

Figure 3.6. Spill pallet with dolly ramp and 30-gallon drums required by Auburn University Risk Management.

WVO drums at the dining facilities are checked and collected approximately eight times per month with the oil transported to the Biosystems engineering biodiesel laboratory. Once in the laboratory, the oil was placed into settling containers (figure 3.7) so particulates from the frying process and any small amount of water can gravitationally settle. Each settling tank had its own pumping system and either tanks' contents could be pumped into the biodiesel processor if desired.

Once the oil has settled for approximately one week, depending upon ambient temperatures, it was pumped from the primary settling tank into the secondary settling tank and allowed to settle for an additional week. Next, the WVO was loaded into the biodiesel processor (figure 3.5) and processed in 208-L batches according to transesterification procedures outlined in Section 3.5 and Section 3.6. After the biodiesel dry wash with AMBERLITE™ BD10, it was pumped into a storage tank (figure 3.8) for future use.

Figure 3.7. Primary (left) and secondary (right) WVO settling tanks.

In addition to the aforementioned components, there are fixed and variable costs associated with the process including: chemicals, PPE (personal protective equipment), spill containment and clean-up equipment, labor, and power requirements. Costs of all components, equipment, processes, and power requirements were evaluated and factored into the economic assessment. Mr. Christian Brodbeck, Research Engineer III, who oversees the biodiesel production system and Mr. Jonathan Griffith, Biosystems engineering technician, were consulted to acquire actual numbers for collection, processing and equipment costs and labor. Typical on-farm labor hourly wage was established by ACES (2011). All fixed costs were given a 10-year life expectancy and straight-line depreciation was used to determine a yearly cost. Lifetime maintenance costs were determined for fixed cost items by calculating 15% of the total cost and dividing by 10 years to determine a yearly maintenance cost. The 2010 total yearly operating cost was divided by total oil collected for 2010 and a cost per gallon was determined.

Figure 3.8. Storage tank for processed biodiesel.

3.9.2 Small-scale, On-farm Biodiesel Production System

Since a small-scale, on-farm biodiesel production system closely paralleling the Auburn University Biosystems engineering biodiesel production system may be feasible; all costs that apply were extrapolated from the previous economic assessment to oilseed crop production data obtained from Section 3.2. From this irrigation experiment, soybeans and canola oilseed data were evaluated.

Data required for economic assessment was adapted from University of Idaho (2010) and included crop yield, oil content, seed storage cost, No. 1 petroleum diesel fuel cost and mechanical press equipment cost plus operating cost. Since the co-product of mechanical pressing of oilseeds is valued as a livestock feed ration supplement, comparable livestock feed prices were gathered as well. Opportunity costs of the oilseeds were used for the economic assessment as it was determined that if a farmer did not produce biodiesel from the oilseeds, he or she would sell the oilseeds through traditional commodity markets.

Once oilseed costs were obtained and yield and oil content determined for each respective oilseed, a cost per gallon of oil was calculated. The oil cost per gallon, in conjunction with the processing

cost from the previous economic assessment and mechanical press operating cost and fixed cost with straight-line depreciation were used to determine a production cost per gallon of biodiesel. Factored into the assessment was a deduction for feed cost, generated by the utilization of oilseed cake as livestock feed supplementation. Biodiesel production cost on a per volume basis was assessed for 2010 monthly averages of commodity market prices of oilseeds and meal. The production costs were compared to No. 1 petroleum diesel fuel costs (ACES, 2011).

3.10 Statistical Analysis

3.10.1 Irrigation Experiment for a Non-traditional Energy Crop Rotation

The trial was designed as a randomized complete block (r=4) with a split plot split block restriction on randomization, where levels of the factor crop rotation were assigned to mainplots, irrigation level to subplots, and crop year was treated as a repeated measures because of the nature of the experiment. For purposes of this study a separate analysis was conducted for each crop because the experiment was too new to be able to investigate rotation effects; the 2nd full cycle of rotation 2 was completed in autumn 2010. The statistical model thus was based on a repeated measures design within a randomized complete block design.

Mixed models procedures as implemented in SAS® PROC GLIMMIX were used to analyze the data, where irrigation treatment, year, and the two-way interaction were fixed effects. Random effects were block, block*irrigation treatment, and block*year. We used R-side modeling to provide for an adequate residual variance structure based on a Corrected Akaike's Information Criterion (AICC). A first-order autoregressive structure that allowed for heterogeneous variances among experimental units [ARH(1)] was appropriate for cotton response variables. No correlated error structure was detected for soybean and canola response variables. This was expected given that these crops were grown on the same experimental unit only every other year. Given that yields varied drastically between crop years

we employed the group option to account for heterogeneous variances between years, again employing AICC to evaluate model fit.

The first step in evaluating the results for a given response variable was to determine if the irrigation treatment x year interaction was significant (α = 0.1). If it was significant then the SLICEDIFF option with a simulation adjustment for multiple comparisons (α = 0.1) was used to compare irrigation treatments within crop years. If the interaction was not significant then the main effect for irrigation treatment was evaluated. Again treatments were compared using the simulation option to guard against an inflated Type I error. Whenever possible the response to irrigation was also modeled using a regression approach within a mixed models framework.

3.10.2 Vegetable Oil Storage Experiment

An analysis of variance (ANOVA) was conducted using SAS's General Linear Model (GLM) to determine possible statistical differences among treatment means for each oil type in Section 3.4. Means were assigned a letter relative to significant differences based on oil type and method of phosphorus removal. Means of the four replications in Section 3.4.1 were plotted (FFA vs. time) and a linear regression analysis was performed, computing a linear equation to predict triglyceride hydrolysis over time. Coefficient of determination was also computed to determine strength of the equation. Mean optical density (absorbance) versus time was graphed using MS Excel at the 550-nm wavelength for each oil type and control samples (Section 3.4.2) to determine microbial accumulation in the oil samples over time. Linear regression analysis of absorbance versus bacteria concentration for positive control samples of oil and water was also conducted with Pearson's Correlation Coefficient calculated to determine linearity among different concentrations.

3.10.3 Methanol Recovery Experiment

Treatment means of methanol recovery in Section 3.5 were computed to determine differences in methanol recovery efficiency (methanol recovered from raw biodiesel and residual methanol in biodiesel post recovery). Means were also generated to determine methanol remaining in glycerol once drained from raw biodiesel. Values were then computed for money saved in recovered methanol to be recycled and money lost in unrecovered methanol.

3.10.4 Biodiesel Quality Experiment

An analysis of variance (ANOVA) was conducted using SAS's General Linear Model (GLM) to determine possible statistical differences among treatment means for biodiesel quality and AMBERLITE BD10 effectiveness in removing free glycerol in Section 3.7.1. Means were assigned a letter relative to significant differences based on treatment and biodiesel sampling time. The ANOVA procedure was also used in Section 3.7.2 to compare means of phosphorus removal methods for soybean oil. Means were assigned a letter relative to significant differences of mean phosphorus removal methods for each oil type. Because canola oil transesterification failed for several treatments, unsummarized data was presented.

3.10.5 Mechanical Extruder Efficiency Analysis

Data from both screw presses were collected measuring oilseed into press and volume of oil out. Time for a mass of seeds or volume of oil to be processed or collected was measured as well. From this data, processing rates and oil output rates could be computed. Knowing the percentage of oil in specific seeds, extraction efficiency was then calculated based on available oil. It was assumed that only 80% of total seed oil was available to be extracted using mechanical means. Data from both presses were compared.

3.10.6 Economic Analysis of Small-Scale Biodiesel Production Systems

Economic analysis of Section 3.9.1 was analyzed in MS Excel by first computing total volume of oil collected on a yearly basis and the associated transportation cost. Next, equipment costs for the collection site and biodiesel production and operating costs were summed, respectively. Each fixed cost component was then given a life expectancy and straight-line depreciation was used to determine a yearly cost. Variable costs were calculated for the year based on the volume of oil collected. The total yearly cost was divided by the total volume of oil processed and the cost per volume was determined. The model structure from Section 3.9.1 was extrapolated to Section 3.9.2 but was adapted to fit an on-farm scenario with components of collection site equipment and portions of the spill containment equipment omitted. In Section 3.9.2, commodity prices were determined from commodity trade reports and a model was generated on an acre basis, taking into account oilseed yield, soyhull pellet price and No.1 diesel fuel price. Yearly costs were calculated with opportunity costs of oilseeds used as the value of the oilseeds. Oilseed cake generated from the extrusion process was given the current market value of soyhull pellets and was recommended to be used as livestock feed ration supplementation. This model was designed in MS Excel to be used by a farmer to assist in predicting his cost per volume of biodiesel production and equipment needed.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Introduction

This chapter reports the results of this study. These results are intended to enhance the understanding of small-scale, on-farm biodiesel production facilities from environmental, feasibility, quality and economic standpoints. Variable irrigation rates on energy crop production was analyzed from both environmental and quality standpoints in determining if seed quality and constituent concentrations were dictated by irrigation levels. Mechanical processing of oilseeds was analyzed for efficiency with collected oil analyzed to ultimately determine best management practices in small-scale biodiesel production to produce consistent quality biofuel. Biodiesel procedures and processes were analyzed for quality measures and process efficiency. Finally, the economics of production systems were estimated to determine feasibility and returns on investments at the farm level.

4.2 Irrigation Experiment for a Non-traditional Energy Crop Rotation

4.2.1 Cotton

Seedcotton yield results showed increased yield with increased irrigation treatments for 2008 and 2010 data (figure 4.1). Given that cotton plots received only 13 cm of seasonal rainfall in 2010 but 29 cm in 2008, the linear regression trend line for 2008 cotton yield data was expected to have been above that of 2010. Total seasonal rainfall at TVREC in 2009 was 32 cm, which was slightly above the 82-year average of 29 cm. However, lower than expected yields for 2009 treatments were attributed to boll shedding due to cool weather and high moisture at the end of the season.

Protein concentration was significantly different among irrigation treatments for the years of the study (figure 4.2). A slight trend was measured for protein concentrations with respect to irrigation treatments in that protein decreased with increasing irrigation levels. Protein levels were reported on a dry matter basis and ranged from 20.5% in 2009 (100% irrigation treatment) to 27.3% in 2010 (25% irrigation treatment). A seven percent protein difference appeared substantial when considering the oilseed cake would be used as livestock feed ration supplementation. However, the overall objective of this experiment was to determine how irrigation might affect biodiesel yield and quality. Protein was a secondary constituent, but yield, the primary constituent effecting biodiesel output, showed favorable results at higher irrigation levels. Therefore, a sacrifice of protein concentrations would be recommended in an effort to increase overall biodiesel yield.

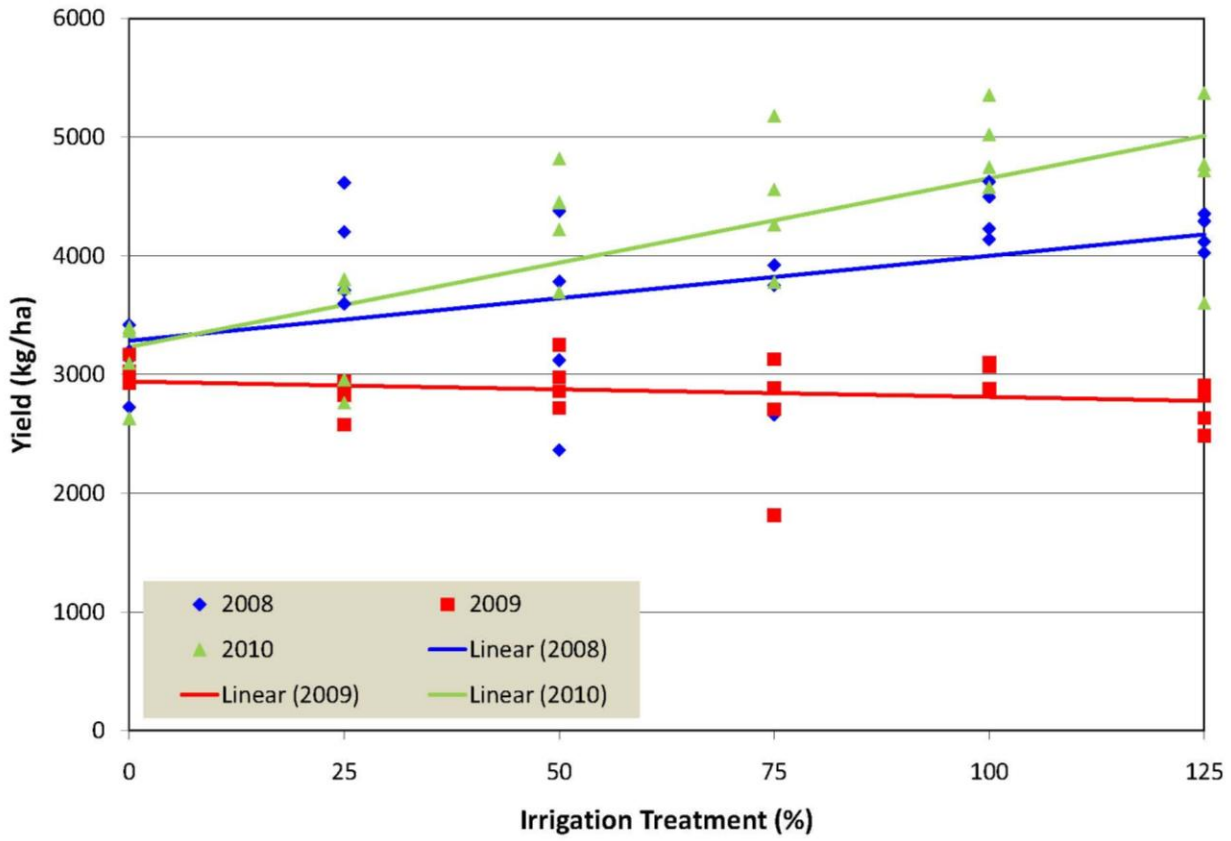

Figure 4.1. 2008 through 2010 cotton yield results.

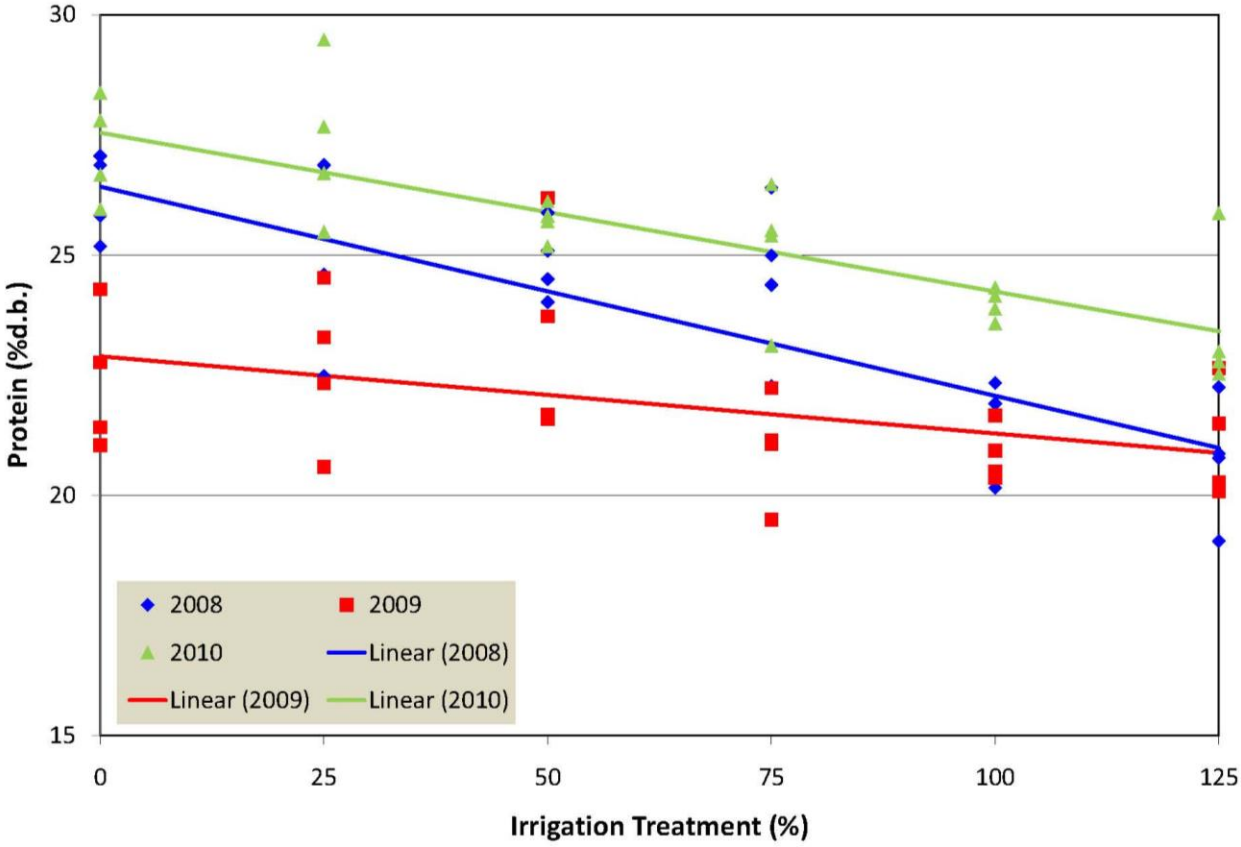

Figure 4.2. 2008 through 2010 cotton protein results.

Figure 4.3. Cottonseed germination inside the boll and prior to harvest, 2009.

The cool weather and high moisture at the end of the season not only effected yield, but also FFA concentrations. FFA levels experienced in 2008 and 2010 were well below 1% for all treatments with yearly averages of 0.6% and 0.4%, respectively. The effect of irrigation on FFA was subtle compared to the biodiesel output limiting factor of yield. For this reason, irrigation treatment recommendations

would be based on yield and not FFA responses. However, the 2009 yearly FFA mean of over 9% was about 18 times higher than 2008 and 2010 means (figure 4.4). Elevated FFA values were attributed to high moisture at the end of the season. The high moisture not only caused boll shedding, but induced seed germination in open cotton bolls (figure 4.3). Late seasonal rainfall resulted in harvest being postponed several weeks after cotton bolls opened. Cottonseeds were exposed to excessive moisture for a prolonged time period and the lipase enzyme in the cottonseed was activated, beginning the germination process. This enzyme initiated the breakdown or hydrolysis of triglycerides in the cottonseed. Through this triglyceride hydrolysis process, energy was released and utilized by the emerging cotton plant with the intention of providing life sustaining nutrients until the root system was established and nutrient uptake along with photosynthesis could begin. The germination process was detrimental in terms of biodiesel production from cottonseeds. With levels of greater than 9%, base catalyzed transesterification alone would be difficult and a quality biodiesel fuel would almost be impossible to produce. Most likely, an acid catalyzed esterification process would be necessary to convert the FFA to esters, thus neutralizing the remaining oil. After the acid catalyzed esterification or acid pretreatment, base catalyzed transesterification could proceed as normal. The acid esterification step would incur substantially more processing costs to a small-scale biodiesel operation. In the event this scenario was experienced on-farm and cotton harvest was prolonged with bolls opened and late season rainfall experienced, a farmer would gain higher returns by selling the seed at the gin.

Cottonseed oil yield in all years of the study resulted in no significant differences among treatments. However as with many of the other parameters, a significant interaction did exist among years. Because year is a non-repeatable variable and considered a “nuisance” factor, year interactions were not discussed. Table 4.1 shows yearly oil concentration means with only 2% difference between lowest and highest years. In terms of biodiesel production, yield was the limiting variable that significantly affected theoretical biodiesel yield. Biodiesel yield, as a result of cottonseed yield response

to irrigation was lowest and highest in 2010 for 0% and 100% treatment means, correspondingly. Irrigation treatments of 0% and 100% pan evaporation adjusted for crop canopy cover resulted in mean theoretical biodiesel yields of 374 L/ha and 620 L/ha, respectively. However, theoretical biodiesel yields in 2009 were not computed due to high FFA concentrations.

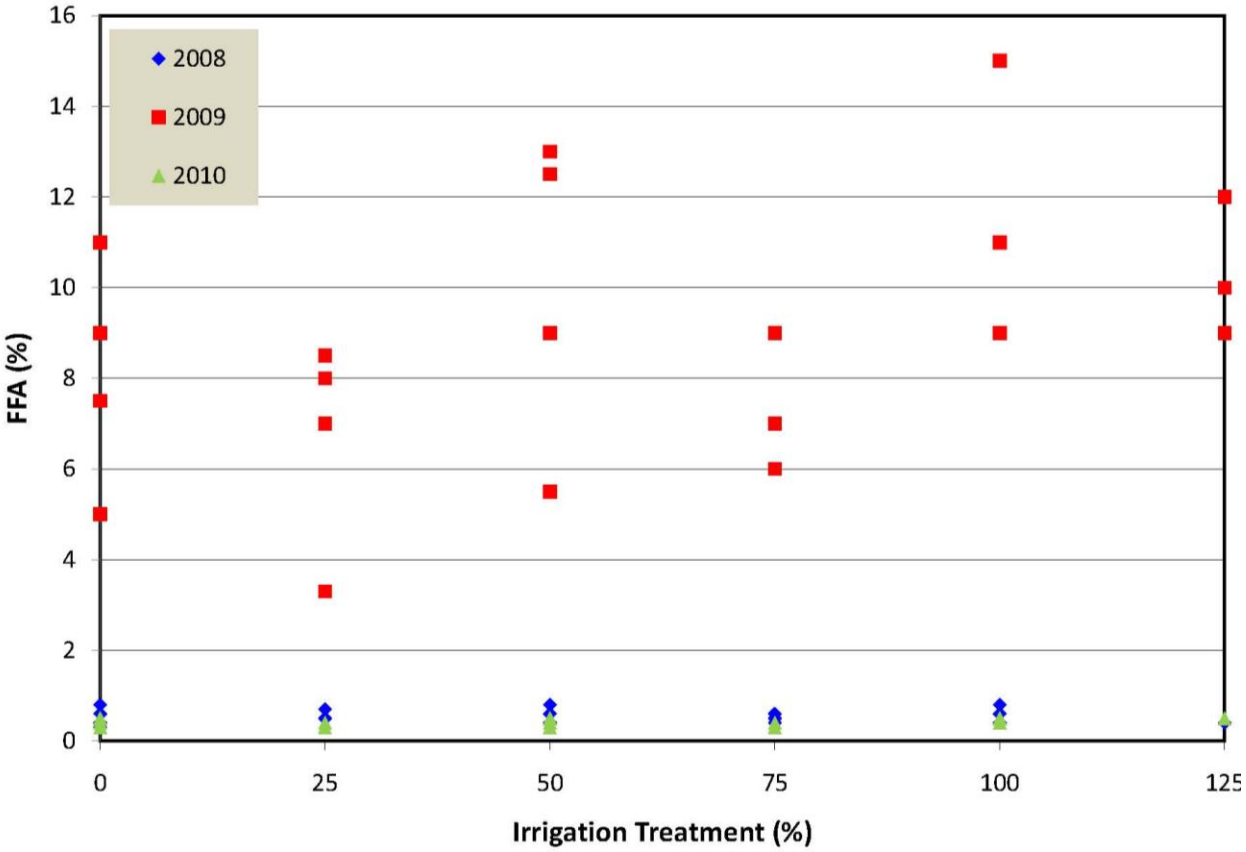

Figure 4.4. 2008 through 2010 cottonseed FFA results.

Table 4.1 2008 through 2010 Cottonseed oil results.

Year	LSmean (%d.b.)*	SE
2008	20.8	0.22
2009	22.4	0.22
2010	22.8	0.22

*d.b. denotes dry matter basis.

4.2.2 Soybeans

Significant differences among treatments were found in soybean for oil and yield, with treatment x year interactions significant except in protein and FFA. Seasonal rainfall (June to August) was 29 cm for soybeans in 2008 but only 13 cm for 2010 soybeans and was valuable in explaining yearly differences for many of the soybean parameters. Figure 4.5 highlights yield results from 2008 and 2010 soybeans. Overall higher yields for all treatments in 2008 were attributed to the seasonal rainfall. However, limited rainfall in 2010 greatly accentuated yield responses to irrigation with the 125% treatment resulting in highest mean yield (4,054 kg/ha). Seed yield proved to be the determining factor

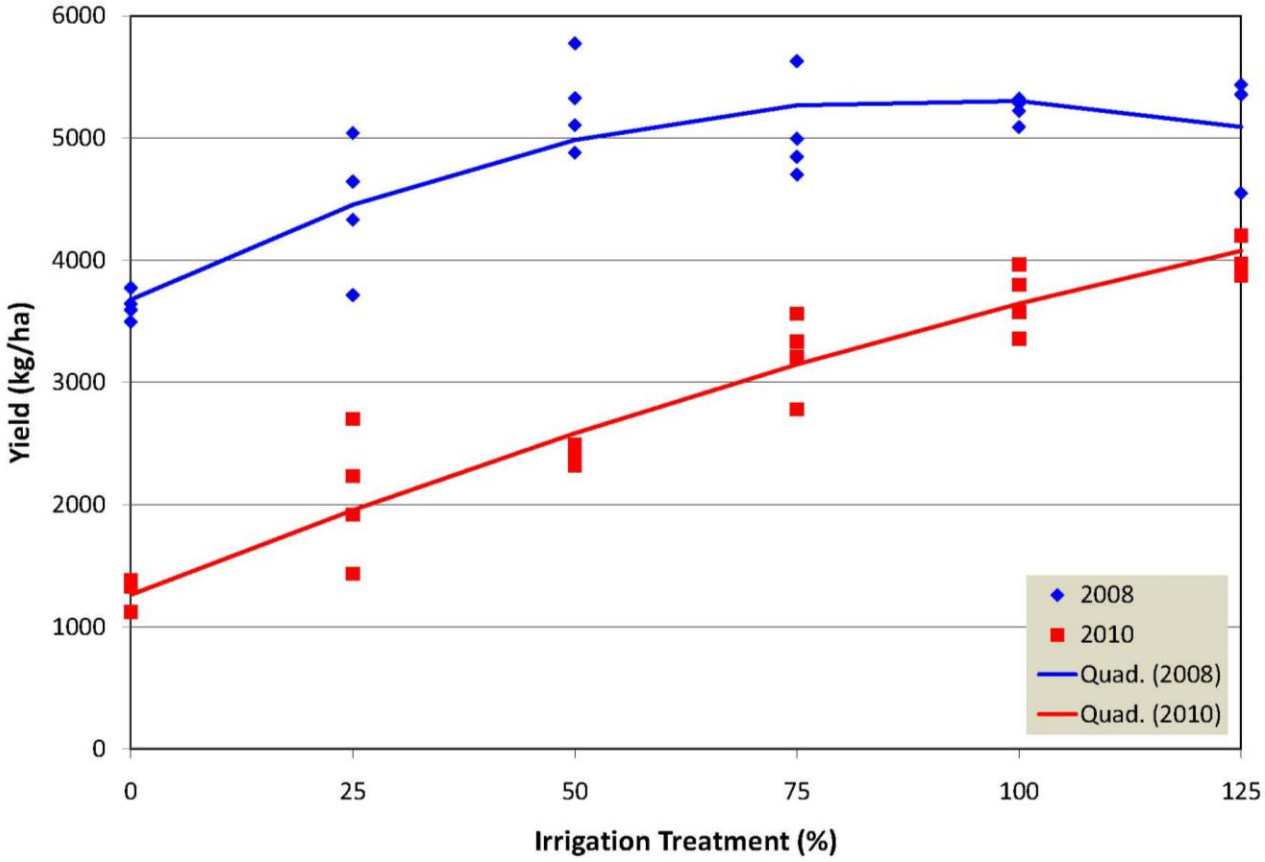

Figure 4.5. 2008 & 2010 soybean yield results.

in biodiesel yield and in years where seasonal rainfall was low, irrigation at 125% pan evaporation adjusted for crop canopy could increase biodiesel yield from 196 L/ha (0% treatment mean) to almost 743 L/ha, as it did in 2010.

Figure 4.6 illustrates lack of interaction between years for protein with quadratic regression lines parallel. Protein was reported on a dry matter basis (d.b.) and increased rainfall in 2008 seemed to explain the difference in quadratic regression lines for protein levels in soybean. Although a difference existed, protein means for 2008 and 2010 only differed by 1.5% which was thought to be negligible in terms of using oilseed cake for livestock feed ration supplementation. However, based on the regression curve, a trend seemed to exist for both years in which 0% treatment means resulted in slightly higher protein concentrations than other irrigation treatments.

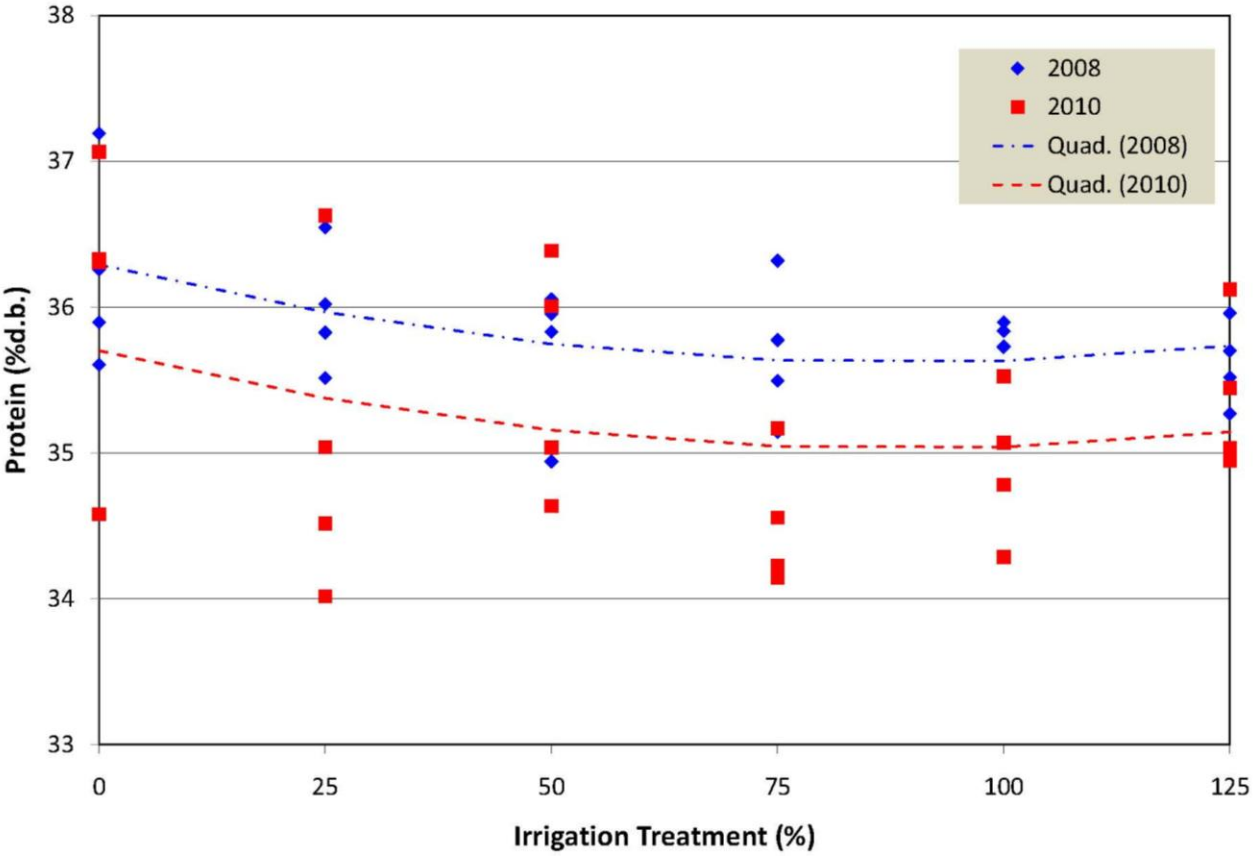

Figure 4.6. 2008 & 2010 soybean protein results.

Oil content showed significant response to irrigation treatments in 2010 (figure 4.7). Given the low seasonal rainfall in 2010, oil content effects due to irrigation were heightened and the 75% irrigation treatment resulted in highest mean oil content. Irrigation treatments of 100% and 125% resulted in similar mean oil levels to the 75% treatment with only 0.3% difference among the three highest treatment means. There was an approximate 2.4% difference between lowest and highest oil concentration means for the six experimental treatments in 2010. If yield was normalized, this would equate to approximately 2.4% more biodiesel per hectare. For the yearly average yield of 2763 kg/ha and average oil content of 20.0%, a difference of 59 L/ha would result from 2.4% more oil.

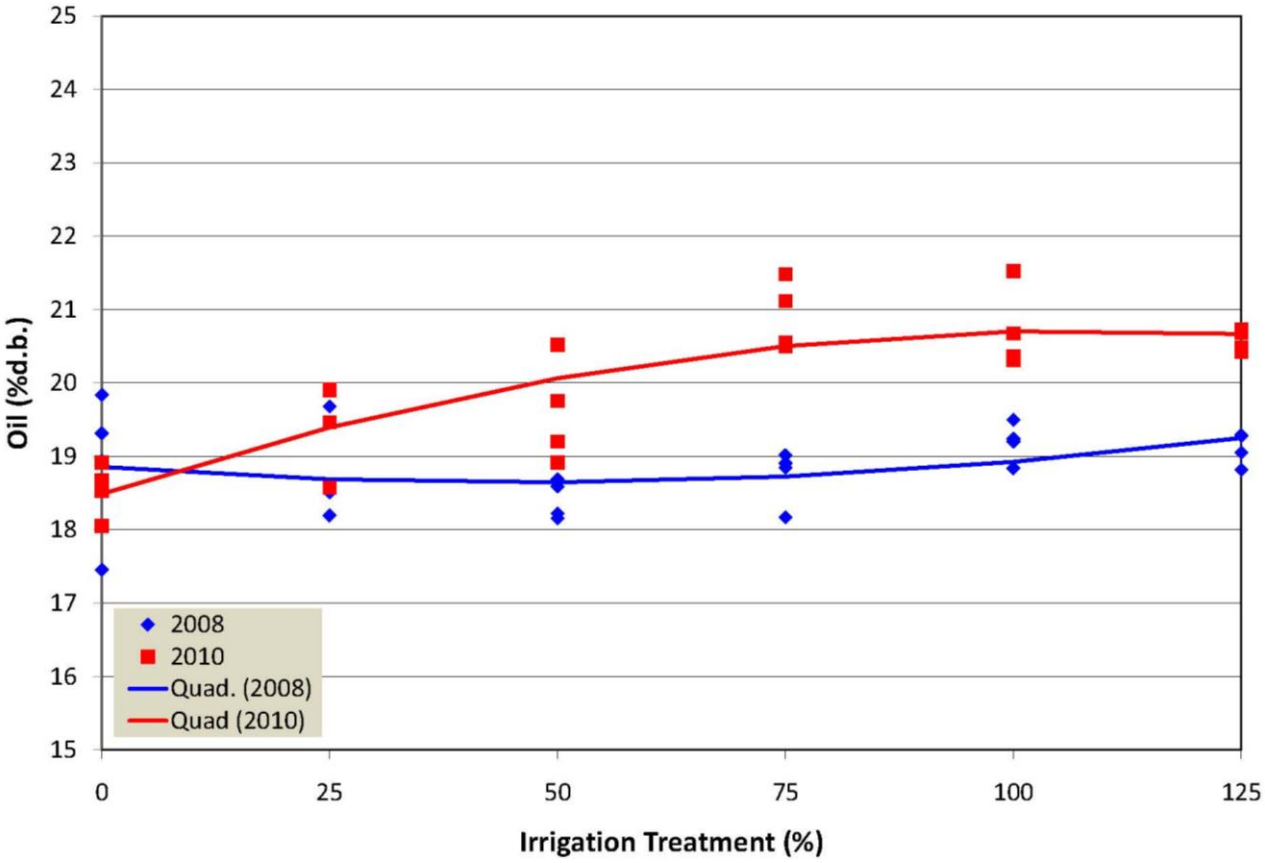

Figure 4.7. 2008 & 2010 soybean oil results.

FFA values for all treatments and both years were not significantly different. 2008 and 2010 mean FFA concentrations were 0.4% and 0.6%, respectively. These values were well below the accepted limit for base catalyzed transesterification (1.0%) and suggested no issues with biodiesel production as a

result of FFA. No soybeans were grown in the experimental energy crop rotation in 2009. However, soybeans were obtained from a farmer in the geographic vicinity of the experimental plots for use in another study. The FFA concentrations of these soybeans were on the order of 20 times higher than those reported in this section. High FFA levels were attributed to conditions experienced in 2009 cotton crop. If soybeans are exposed to these extremely wet conditions once the beans are fully formed, base catalyzed transesterification will most likely be difficult to effectively perform, thus resulting in poor quality fuel or conversion failure.

4.2.3 Canola

Table 4.2 highlights results of canola to crop rotation. Because canola was grown as a winter crop, no irrigation was applied post emergence. Differences were expected to be as a result of rotation; thus, no effects as a result of irrigation treatments were found during the study. For this experiment, canola was grown two different years, and no significant differences were attributed to the fact that the experiment was too recently established to investigate effects of rotation. Therefore, LSmeans and standard error were reported on a yearly basis for each parameter.

Average canola yield in 2010 was over double 2008 mean yield. Rainfall data during the 2007-2008 canola growing season (November to May) was 67 cm as opposed to 84 cm for 2009-2010 growing. FFA difference between years was only 0.3% on average and in terms of biodiesel production, both years FFA concentrations were acceptable to achieve satisfactory ester conversion. Oil and protein differences were similar between years as well. Thus, yield was the limiting factor in biodiesel production on an area basis. In 2010, theoretical biodiesel yield was 1,026 L/ha, with only 517 L/ha calculated for 2008. Because year was considered a nuisance factor and cannot be repeated, differences in canola yield were attributed to rainfall; ultimately resulting in substantial theoretical biodiesel yield difference among years.

Table 4.2. 2008 & 2010 canola results.

	2008		2010	
Parameter	**LSmean**	**SE**	**LSmean**	**SE**
Plant density, plants/ha	1,388,096	134,497	1,232,827	90,677
Yield, kg/ha	1293.3	128.1	2673.2	119.9
FFA, %	0.8	0.1	0.5	0.0
Oil, dry matter basis, %	44.9	0.3	43.1	0.2
Protein, dry matter basis, %	24.5	0.1	22.7	0.2

4.2.4 Irrigation Summary

Experiments of Sprecht et al. (2001), Sims et al. (1993), and Ibrahim and Kandil (2007) found that oil concentration decreased or remained unchanged with irrigation. Results of this study showed similar oil concentration ranges, however, oil concentration increased with irrigation during 2010. Protein concentrations decreased with increasing irrigation in soybeans and cotton; a finding that contrasted Boydak et al. (2002), Bellaloui and Mengistu (2008), and Ibrahim and Kandil (2007). Although as with oil concentration, overall percentages were within the range of other experimental studies. Lee et al. (2008) and Boydak et al. (2002) found that irrigation had no significant effect on FFA. Conversely, Taylor et al. (1991) reported that rainfed conditions increased FFA. Both scenarios were found in this study with 2009 cotton showing highest FFA for 0% irrigation. Nevertheless, all researchers agreed that yield was positively influenced by irrigation but that cultivar differences, growing season, geographic location, and agronomic practices all impact oilseed constituents (Boydak et al., 2002 and Bellaloui and Mengistu, 2008).

4.3 Review of Biodiesel Production Procedures

Table 4.3 provides a partial list of various biodiesel production methods that have been investigated in terms of cost effectiveness while meeting a desired conversion efficiency of 95%. These production methods were gathered from various literature in an attempt to determine the most feasible method that a farmer could utilize. The table was ordered based on chemical expense with the assumption that a farmer's most inhibiting factor would be production cost. Results were normalized for

a 208-L batch of biodiesel but did not include overhead, equipment, or operational costs. The variability of these costs was difficult to ascertain as they may differ from farm to farm. From these results, the best-practice method could be interpreted in several ways. No data was included that resulted in an ester conversion efficiency lower than 95%, but if conversion efficiency is the most desired factor of biodiesel production, 1 wt% sulfuric acid with a 9:1 molar ratio of methanol to oil may be the preferred method of production. These levels provided the highest ester conversion efficiency of 99% after a 19-hour reaction time at a cost of $0.24/L. While this method seems to yield the highest ester concentration, it has a relatively long reaction time per batch and may lead to engine corrosion if trace amounts of sulfuric acid remain in the biodiesel during use. Several methods reported reaction times as short as one hour; however, they are not equal in other regards. Base catalyzed transesterification seems to, on average, require the shortest reaction times.

Table 4.3. High ester yielding biodiesel production procedures with low chemical costs.

Catalyst	Amount (%)	Alcohol	Amount (MR)*	Reaction time (hr)	Conversion rate (%)	Chemical cost/liter ($)†	Researcher‡
NaOH	1	methyl	6:1	4	>96	0.16	a
	0.3	ethyl	12:1	1	97.2	1.31	d
KOH	1.4	methyl	6:1	4	>96	0.21	b
	1	ethyl	12:1	1	95.6	1.35	d
	1.07		20:1	NA	98	2.22	e
H_2SO_4	1	methyl	9:1	19	99	0.24	c
	3		6:1	96	95.1	0.25	c
	5		6:1		95	0.33	c
	3		20:1	48	96	0.56	c
	3		30:1		98.4	0.79	c
	3	ethyl	6:1	48	95.8	0.77	c

*MR denotes molar ratio of alcohol to oil

†based on 2010 chemical costs in Alabama

‡Freedman et al., 1984a[a]; Coteron et al., 1997[b]; Canakci and Van Gerpen, 1999[c]; Kucek et al., 2007[d]; Joshi et al., 2008[e]

Sodium hydroxide or potassium hydroxide at an amount of 0.3% and 1%, respectively, coupled with ethyl alcohol at a molar ratio of 9:1 seems to require the shortest reaction times that yield >95%

ester conversion with a cost ranging from $1.31 to $1.35/L (price based on 2010 chemical cost). With only a 3 hour longer reaction time and an ester conversion efficiency closely correlating to the prior method, 1% NaOH with 6:1 molar ratio of methanol to oil or 1.4% KOH with 6:1 molar ratio of methanol seems to be the most viable option for an Alabama farmer. The cost associated with each of these methods would be $0.16/L or $0.21/L for a 208 L batch, respectively.

According to Freedman et al. (1984a) a 6:1 molar ratio of alcohol to oil should be used. Ratios greater than this value do not increase yields, however, they complicate ester and glycerol recovery, and add costs to alcohol recovery. From table 4.3, two methods using a 6:1 molar ratio of methanol to oil appeared to be the most economic and yield conversion efficiencies >96%. Freedman and Pryde (1982) reported that acid catalysis was much more effective than base catalysis when FFA levels exceed 1%.

Base catalyzed transesterification seems to be the most feasible method of biodiesel production for an average Alabama farmer because of its relative ease and cost. While Joshi et al. (2008) determined that FAEE (fatty acid ethyl ester) may have enhanced low temperature properties in comparison to FAME (fatty acid methyl ester) and that a maximum yield of 98% ester could be obtained at a KOH level of 1.07% wt/wt and ethanol to oil ratio of 20:1, it may not be the most feasible for a farmer. This method may work for a farmer who has access to ethanol, but in Alabama, methanol is incomparably cheaper with comparable results to that of using ethanol.

Coteron et al. (1997) found that a KOH level of 1.4% wt/wt produced the optimal ester conversion efficiency but any concentration greater, produced lower ester yields because of the presence of soaps, which prevents ester layer separation. From a cost perspective, this method was feasible, though not the most economical. NaOH seems to perform comparably at a more desirable cost. However, ester yield may be increased with a method reported by Bradshaw (1942) in which alcohol was added in three or four portions to obtain a 98% ester yield. He found that a three to four step reaction could aid in alcohol molar ratio reduction from 4.8:1 to 3.3:1. Bradshaw (1942) along with other

researchers noted that molar ratios greater than 5.25:1 or 6:1 interfered with gravity separation of the glycerol and added useless expense to the separation (Fuege and Gros, 1949; Gauglitz and Lehman, 1963; Lehman and Gauglitz, 1966). These studies also found that NaOH catalyst increased from 0.2%-0.8% at 6:1 molar ratio of methanol liberated significantly more glycerol yield. Similarly, Freedman et al. (1984a) found that 1% sodium hydroxide at FFA concentrations less than 0.5% yielded 96% to 98% conversion for methyl alcohol in 1 hr. While this result may not be the case for all oilseeds in this experiment, it seems to be a feasible option for soybeans and possibly cottonseed with achievable ester yields between 96% and 98% by simply increasing the reaction time several hours.

Table 4.4 provides a partial list of biodiesel production methods published by researchers that was investigated in this study. A complete list can be viewed in Appendix A. These methods met the desired criteria of 95% conversion efficiency although all methods are not necessarily recommended as best practice methods. When these methods were analyzed by oil type, it was obvious that soybean oil has been the most widely researched oil type. That can be attributed to the fact that soybean is the most frequently oilseed crop grown in the US for food purposes and thus researched for possible biodiesel production. The highest conversion efficiency (98.4%) was experienced when using a 30:1 methanol to oil molar ratio and 3.0% sulfuric acid catalyst, a reaction time of 48 hours and a reaction temperature of 60 ^{o}C. Generally, most studies obtained similar results with a more conservative molar ratio of 6:1 and similar practices to this method in terms of reaction temperature and duration. For instance, when using a cheaper, less harmful chemical like sodium hydroxide, 98.0% conversion efficiency was obtained for soybean oil using 1.0% sodium hydroxide, a 6:1 molar ration of methanol to oil, reaction time of 4 hours and reaction temperature of 60 ^{o}C. When reducing the reaction time of this exact experiment to one hour, only one percent drop in conversion efficiency was experienced. When considering the utility requirement for the additional three hours of reaction time, the advantage was negated. Likewise, another study used one percent sodium hydroxide, 6:1 molar ratio of methanol to oil,

reaction temperature of 45 ^{o}C and reaction time of one hour and found a 97% ester conversion in soybean oil. The reduction in temperature of 15 ^{o}C for this scenario has the potential to drive the cost of processing down even further, excluding the fact that methanol and sodium hydroxide are the least expensive input chemicals for transesterification in the southeast US. Similarly, 0.5% sodium methoxide

Table 4.4. Published biodiesel production procedures based on oil type.

Oil Type	Catalyst type (wt.%)	Alcohol (MR)*	Reaction time (hr)	Reaction Temp. (C)	Conversion Efficiency (%)	Researcher‡
Soybean	NaOH (0.3)	EtOH (12:1)	1	30	96.8	1
				70	97.2	
	NaOH (0.65)	EtOH (9:1)	1	50	95.8	1
	NaOH (1.0)	MeOH (6:1)	0.2	60	95.0	3
			0.5		96.0	
			1		96.0	
			2	32	96.0	3
			4		98.0	
			20		98.0	
	$NaOCH_3$ (0.5%)	MeOH (5:1)	1	60	95.0	3
		MeOH (6:1)	0.5	60	97.0	3
			1		98.0	
	KOH (1.0)	EtOH (12:1)	1	30	95.1	1
				70	95.6	
	H_2SO_4 (1.0)	n-BuOH (30:1)	3	114	95.0	3
	H_2SO_4 (5.0)	MeOH (6:1)	48	60	95.0	2
			96		95.1	
		MeOH (20:1)	48	60	97.0	2
		MeOH (30:1)			98.4	
		EtOH (6:1)	48	75	95.8	2
Sunflower	$NaOCH_3$ (0.5%)	MeOH (6:1)	1	60	98.0	3
		EtOH (3:1)	0.5	75	95.0	3
		EtOH (6:1)	1		97.0	
		n-BuOH (6:1)	1	114	95.0	3
Peanut	$NaOCH_3$ (0.5%)	MeOH (6:1)	1	60	97.0	3
Cottonseed	$NaOCH_3$ (0.5%)	MeOH (6:1)	1	60	95.0	3
Canola	$KOCH_3$ (1.59)	MeOH (4.5:1)	0.167	50	95.8	4

*MR denotes molar ratio of alcohol to oil

‡Kucek et al., 2007[1]; Canakci and Van Gerpen, 1999[2]; Freedman et al., 1984a[3]; Singh et al., 2006[4]

was used for soybean oil transesterification at 6:1 molar ratio of methanol to oil, reaction temperature of 60 ^{o}C and reaction time of 1 hour with 98% conversion efficiency, however, sodium methoxide was a

bit more cost prohibitive as opposed to sodium hydroxide. Advantages of sodium methoxide will be discussed next.

Sunflower oil was the second most frequent oil type to appear in published literature reviewed. Sodium methoxide was used as the catalyst in experiments outlined. It was determined that 98% conversion efficiency could be experienced as a result of 0.5% sodium methoxide, 6:1 molar ratio of methanol to oil, reaction time of one hour and reaction temperature of 60 ^{o}C. These results fair favorably to the soybean oil results. Of interest, some researchers chose to use sodium methoxide as opposed to sodium hydroxide. When methanol and sodium hydroxide are mixed in a transesterification reaction vessel, water can be a product of the reaction to form sodium methoxide as the methanol has the potential to be slightly acidic. Water was also a transesterification inhibitor as reported by multiple researchers. Freedman et al. (1984a) selected chemical grade sodium methoxide purchased from a commercial source as the catalyst in their study because the water had already been removed and was not a potential inhibitor of the reaction.

Several methods of transesterifying peanut, canola and cottonseed oil were investigated and can be viewed in Appendix A, however, only one method for each oil type met the 95% conversion efficiency threshold required for the developed list. Of particular interest was the catalyst used for canola oil in table 4.7. Singh et al. (2006) used potassium methoxide at a concentration of 1.59% and methanol at a molar ratio of 4.5:1 to oil. The reaction time was only 10 minutes and the resulting conversion efficiency was surprisingly almost 96%. However as previously stated, sodium hydroxide is still the cheaper catalyst with similar results experienced at a longer reaction time. A similar reaction, which did not qualify for inclusion in table 4.7, used soybean oil with 1.0% sodium hydroxide at a reaction temperature of 60 ^{o}C, 6:1 molar ratio of methanol to alcohol and reaction time of 6 minutes. This method required less time than the previously discussed reaction, but yielded only 94% conversion.

4.4 Vegetable Oil Storage Experiment

4.4.1 Triglyceride Hydrolysis

Once soybean oil and canola oil samples were mechanically extruded and WVO collected for this experiment, all four replications of each oil type were initially tested for water content. It was known that water content could have adverse effects on vegetable oils and could expedite triglyceride hydrolysis (FFA accumulation) in the experimental samples. Table 4.5 reports the initial water content results. Control samples were also tested for water content after autoclaving for sterilization. These results are not shown; however average water content was not significantly different in the control samples after they were autoclaved.

During the approximate nine months of vegetable oil storage in four-liter HDPE sealed containers, WVO showed the highest percentage increase of FFA, approximately 68%. Surprisingly, soybean oil followed with approximately 50% FFA increase and canola oil resulted in least percent FFA increase, 43% (figure 4.8). Statistical analysis of the data revealed that slopes of each oil type were significantly different ($p<0.0001$). Each oil type oxidized at a different rate. Linear regression indicated a strong correlation existed for WVO and canola oil. The linear equations of FFA hydrolysis over time can be used with confidence in predicting hydrolysis of stored WVO and canola oils in sealed, airtight HDPE containers.

Researchers typically recommend biodiesel feedstock FFA concentrations below 2%. Only soybean oil was consistently below 2% for the duration of this experiment. WVO and canola oil FFA concentrations initially were 2.8% and 2.3%, respectively. On the other hand, canola oil biodiesel data from Section 4.7.2 may suggest that these elevated FFA concentrations in WVO and canola oil could be acceptable for base catalyzed transesterification and still yield a relatively high quality fuel. Although some replications of canola oil failed during the transesterification experiment, the highest FFA

concentration experienced in this experiment was approximately 40% lower for WVO and 200% lower for canola oil than experienced in the degummed oil transesterification experiment. However, it was speculated that additional factors, besides FFA concentration alone, led to transesterification failure in canola oil samples in the degummed oil transesterification experiment. Still, all 10 canola oil samples that were drawn from the top layer of the semi-sealed storage container with average FFA concentration of 6.2% transesterified.

Table 4.5. Initial water content of samples for the oil storage experiment.

	Water (wt%)	
Sample	**Mean**	**SD**
Canola oil	0.71	0.18
WVO	1.05	0.54
Soybean oil	0.84	0.40
Canola oil control	0.42	0.16
WVO control	1.30	0.08

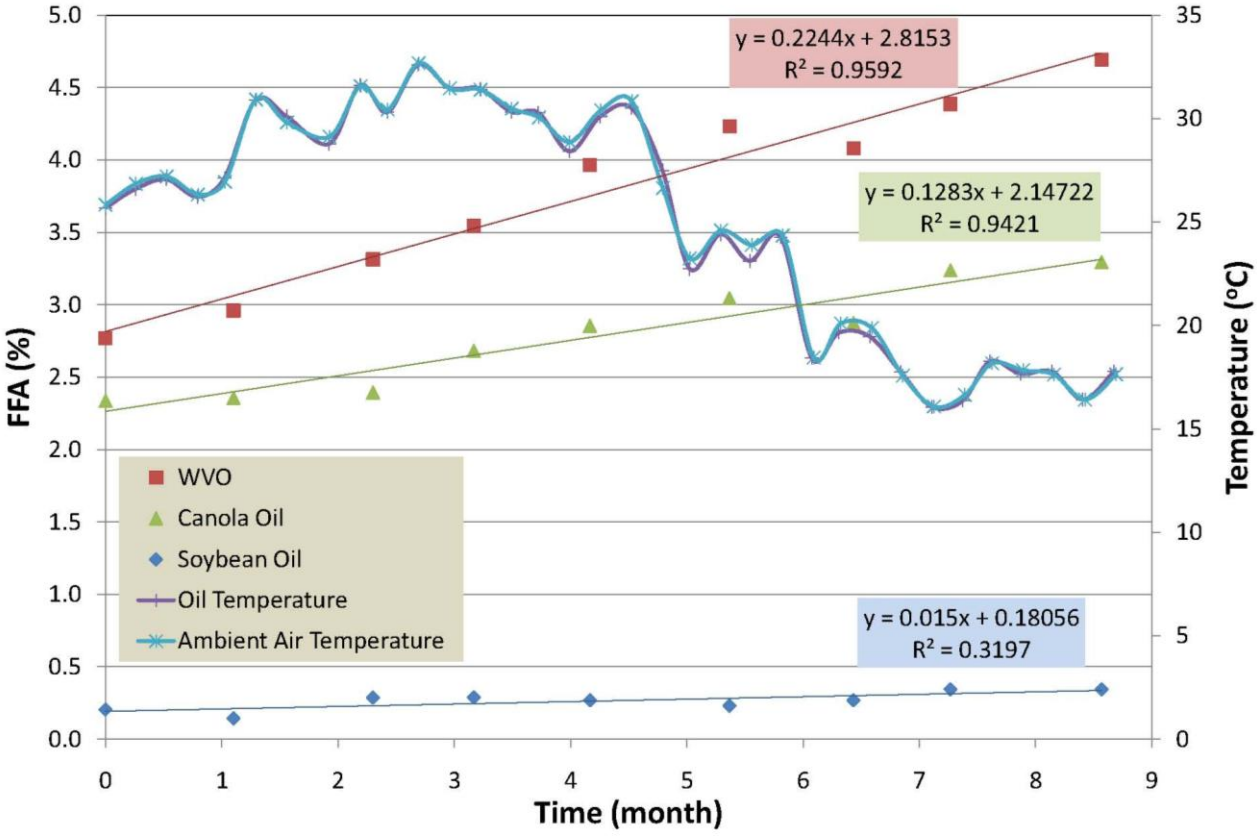

Figure 4.8. FFA accumulation in vegetable oil samples over time.

Of noteworthy importance was the difference in FFA concentrations of canola oil in both experiments. Although this level was not a factor in the experimental designs of either experiment, it was interesting to observe these differences. On average FFA concentration in canola oil during this storage experiment did not exceed 3.3%. However, average FFA concentration of the canola oil control samples in Section 3.7.2 were 100% greater. These canola oil samples were from the same batch of oilseeds, seeds were stored for the same duration, oil was mechanically extruded the same day, and oil was stored for the same duration in the same environment. Yet, vegetable oil storage samples were stored in sealed, air-tight HDPE containers and oil for the degummed oil transesterification experiment was stored in semi-sealed containers that were not as air-tight as the HDPE four-liter jugs.

4.4.2 Microbial Contamination

Data analysis for this experiment provides relative absorbance measurements over time. Relative absorbance measurements are due to the fact that repeatability is heavily dependent on the volume of sample tested. Several tests during this experiment resulted in slightly different volumes tested due to pipette models used, thus highly repeatable results were not obtained. However, relative absorbance measurements at 550-nm wavelength indicated that over time, absorbance did not change significantly (figure 4.9). In vegetable oil samples of soybean, canola, and waste oil, absorbance values remained relatively the same and even dropped slightly as storage time progressed. Also, control samples of WVO and canola oil resulted in absorbance values not significantly different from non-control samples. This result indicated that there was no microorganism activity in the oil samples prior to storage, which was an expected result. De-ionized water analysis with the ultra-violet spectrophotometer produced consistent results over the storage period. This consistency led to the conclusion that the machine was providing steady readings throughout the duration of the experiment.

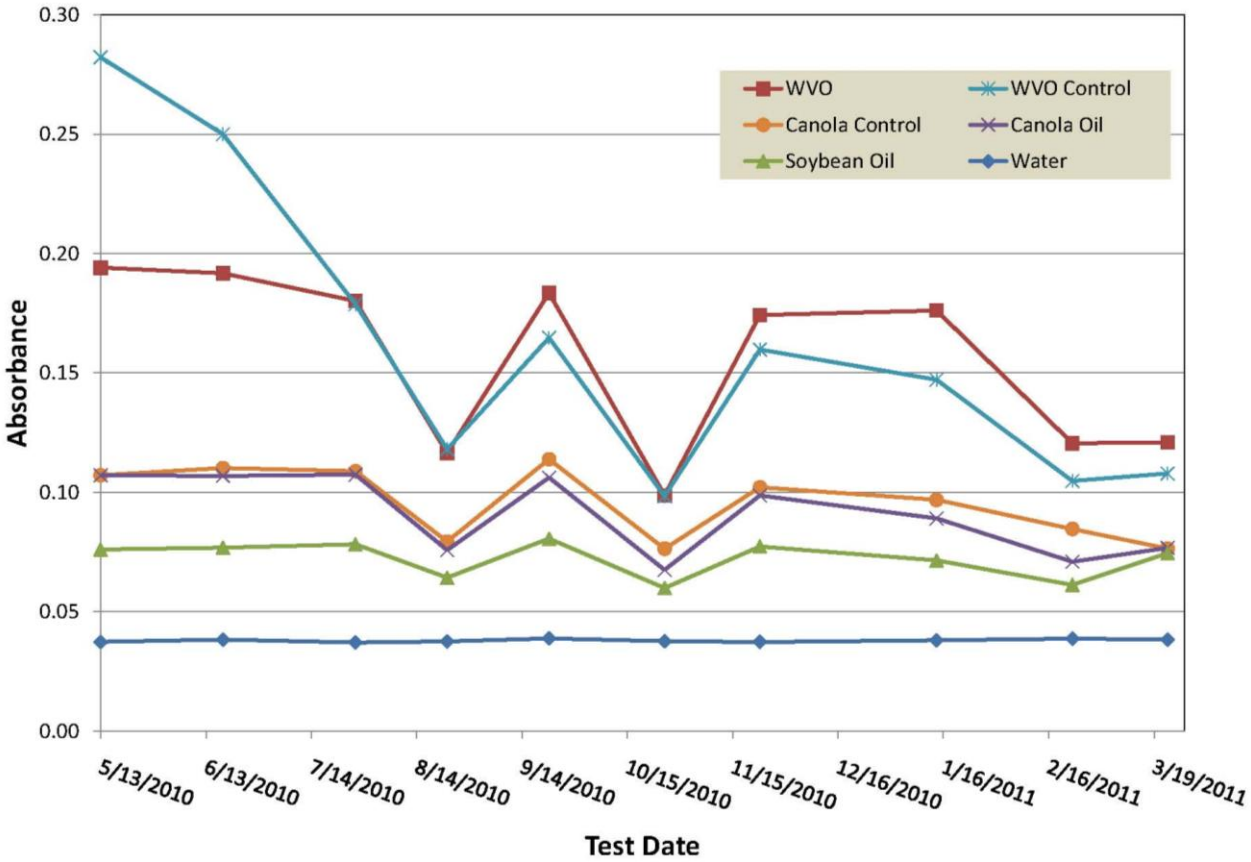

Figure 4.9. Experimental sample data from absorbance testing over time.

Figure 4.10 illustrates bacteria positive control analysis at 550-nm wavelength in water and WVO. If the experimental samples had contained microorganisms, increasing absorbance peaks at 550 nm would have been expected that might have correlated somewhat to the positive control graph. Also, the equation of the linear regression fit from this graph would have allowed for calculation of the concentration of microorganisms in the experimental samples with high coefficient of determination (r^2 0.9491).

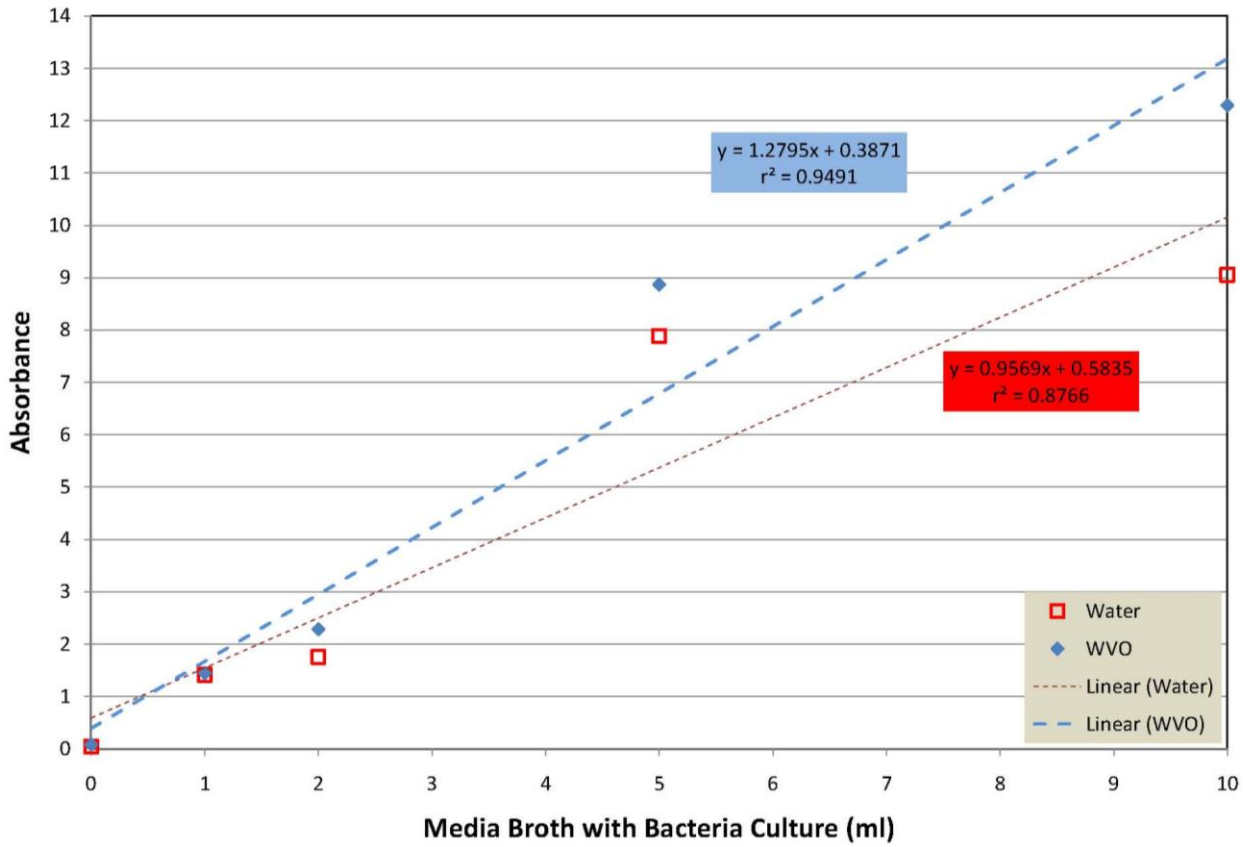

Figure 4.10. Bacteria positive control sample analysis from absorbance testing

4.5 Methanol Recovery Efficiency Experiment

The methanol recovery experiment was conducted with two treatments 1) standard practice method of methanol recovery recommended by the manufacturer and 2) vacuum pump assisted methanol recovery, creating negative pressure to encourage methanol vapors to move to the condenser and be recovered as liquid methanol. To ensure the accuracy and repeatability of the evaporative method, a control experiment was performed first. Table 4.6 reports the results from this method. Samples similar to experimental samples were chosen as control samples with the tests replicated three times. Changes in initial weight and final weight resulted in only 0.38% error for the worst scenario. From these results, it was determined that this method could provide reasonably accurate results in determining methanol concentrations from experimental samples.

Table 4.6. Evaporative method reliability for methanol determination.

	-------Initial Values-------					Calculated final values	
Rep*	RBD oil (g)	MeOH wt. (g)	Total (g)	MeOH (%)	Final wt. (g)	MeOH wt (g)	% Error
1	37.51	12.46	49.97	24.93	37.53	12.44	0.16
2	37.60	12.65	50.25	25.17	37.56	12.69	-0.32
3	37.20	13.09	50.29	26.03	37.15	13.14	-0.38
Mean	37.44	12.73	50.17	25.38	37.41	12.76	-0.18
SD	0.21	0.32	0.17	0.58	0.23	0.35	0.30

* Samples were Refined, Bleached & Deodorized (RBD) canola oil + methanol

Table 4.7 illustrates the average amount of methanol contained in different phases of the transesterification reaction, methanol recovered from raw biodiesel and the monetary gain or loss as a result of recovery. It was determined that of the 17.9 L of methanol added to the WVO for transesterification, approximately 10.6 L were consumed by the reaction for the formation of fatty acid methyl esters. The theoretical consumption of methanol for a 90-L batch is 10.9 L, not significantly different from the average calculated consumption. On average, 7.3 L of methanol remained in the biodiesel/glycerol mixture with almost 40% of that volume was drained off with the glycerol layer in the biodiesel prior to methanol recovery (table 4.7).

Ideally, methanol should be recovered from the glycerol layer as well to retain maximum efficiency in the process and in order to recycle the methanol to future batches. However, from the evaporative experiment, glycerol in the absence of methanol became extremely viscous and cleaning the round bottomed flask for use with the next evaporative sample was difficult as the glycerin solidified and adhered to the flask. Likewise, after it was determined that vacuum pump assisted methanol recovery proved beneficial in recovering methanol from biodiesel, the method was employed by Auburn University Biosystems engineering staff. Apparently small amounts of glycerol that were not drained with the initial glycerol and/or a minute amount of post reaction occurred during methanol recovery. After the raw biodiesel cooled from the recovery process, the piping infrastructure became clogged

from this coagulated glycerin and required heating to dislodge the solidified glycerin and free the piping system to continue the process. Methanol recovery prior to draining glycerol appears to be a simple resolution to recover maximum amounts of methanol, but for the reasons mentioned earlier, it is not recommended. An alternative methanol recovery from glycerol once removed from the reactor would be advantageous in recovering excess methanol for recycling.

Vacuum pump assisted methanol recovery resulted in an average 600% increase in methanol recovered as opposed to the standard procedure. Also, this removed residual methanol from the biodiesel which would have otherwise lowered the flash point and could have caused safety issues when storing and using biodiesel in an engine. Residual methanol in biodiesel was lowered by 380% on average when using the vacuum pump assisted methanol recovery.

Also highlighted in Table 4.7, are the economics of methanol recovery as a result of the two treatments. An average methanol savings of $1.28 per 90-L batch was experienced when using vacuum pump assistance versus standard recovery procedures. However, an average of $1.39 was lost with the standard methanol recovery procedure that could have been recovered with the vacuum pump assistance method. The average cost of operating the biodiesel processor for one 208-L batch, typical amount processed, with vacuum pump assistance was estimated at $1.36. When considering that $1.28 was saved with vacuum pump assistance, the cost of processing a single batch can almost be retrieved in the recovered methanol that can be recycled for future use.

Table 4.7. Volumetric balance and economic analysis of methanol recovery experiment.

		Treatment		
		Standard	Vacuum	Difference
Methanol in glycerol (L)	Mean	4.31	4.45	0.14
	SD	0.18	0.35	
Methanol recovered from raw biodiesel (L)	Mean	0.41	2.46	2.05
	SD	0.18	0.22	
Residual methanol in biodiesel post recovery (L)	Mean	3.04	0.80	-2.24
	SD	0.15	0.14	
Dollars lost in unrecovered methanol*	Mean	$1.89	$0.50	($1.39)
	SD	$0.09	$0.09	
Dollars saved in recovered methanol*	Mean	$0.25	$1.53	$1.28
	SD	$0.11	$0.14	

*Power usage not calculated but considered negligible.

4.6 Phosphorus Removal from Vegetable Oil Experiment

Both crude extruded soybean and canola oils were degummed with one of three experimental treatments: hot water, citric acid or anion exchange resin. Oils in this experiment were extruded and stored in semi-sealed HDPE containers for approximately 7-8 months before degumming to simulate an actual on-farm scenario. There was a control group to verify phosphorus removal efficiency. Table 4.8 provides the results of phosphorus removal from canola oil. The canola control mean phosphorus content was 51 ppm, which was not significantly different than degumming treatments of hot water and anion exchange resin. However, degumming canola oil with citric acid proved to consistently decrease phosphorus content in canola oil by almost 50%. Lowest levels of phosphorus using citric acid treatment can be attributed to the fact that hot water and citric acid were used for the citric acid treatment as outlined by Brekke (1980). Hot water has been believed to remove hydratable phospholipids of the vegetale oil whereas citric acid will remove non-hydratable phospholipids. When hot water and citric acid methods are compared, it appeared a larger majority of the phospholipids removed from the canola oil were non-hydratable and as a result were removed with citric acid and not in the hot water treatment. ASTM Standard D 6751 (2007) requires phosphorus

content in biodiesel to be ≤10 ppm and citric acid treatment alone remained unsatisfactory in meeting the standard requirements.

Table 4.8. Results of phosphorus removal from canola oil.

	Phosphorus content (ppm)	
Treatment	**Mean†**	**SD**
Control	51 a	1
Citric acid	26 b	2
Hot water	49 a	3
Anion exchange resin	47 a	1

† Means designated by the same letter are not significantly different (P<0.05).

Phosphorus removal in soybean oil seemed to be more favorable in oil responses to treatments (table 4.9). However, the soybean oil control mean was initially lower than canola oil. Each treatment was significantly different than the others, indicating that each had a significant impact on phosphorus removal within the soybean oil. As with canola oil, if hot water and citric acid treatments are compared, citric acid outperformed the hot water treatment. Likewise, this difference can be attributed to the fact that the citric acid treatment called for hot water and citric acid, removing both hydratable and non-hydratable phospholipids. The lowest phosphorus content (24 ppm) was attained with the anion exchange resin, unlike canola oil; however citric acid results for each oil type had similar means.

It was unclear why the anion exchange resin was successful at removing almost five times more phosphorus in soybean oil as compared to canola oil. The anion exchange resin was advertised by the manufacturer as being capable of removing proteins, phospholipids and cations. Cations can exist as FFA and FFA values in experimental canola oil samples were almost 1700% higher than experimental soybean oil samples. However, the anion exchange resin was successful in reducing FFA in soybean and canola oils by 30% and 22%, respectively. FFA differences were a result of 7-8 months of storage in semi-sealed HDPE containers, simulating an on-farm scenario. Anion exchange resin performance differences between oil types may possibly be attributed to higher FFA concentrations in canola oil, thus resulting in

poor phosphorus removal from canola oil. Protein content in each oil type was not known, but suspected to have an insignificant impact on anion exchange resin performance.

Table 4.9. Results of phosphorus removal from soybean oil and biodiesel.

Treatment	Phosphorus content in oil (ppm)		Phosphorus content in biodiesel (ppm)		Difference (ppm)
	Mean†	SD	Mean†	SD	
Control	45 a	1	24 ab	1	21
Citric acid	27 c	0	23 ab	1	4
Hot water	32 b	1	29 a	5	3
Anion exchange resin	24 d	1	22 b	0	2

† Means designated by the same letter are not significantly different within columns (P<0.05).

Samples of WVO collected from Auburn University dining facilities were also tested for phosphorus content. These oils were commercially refined, bleached, and deodorized (RBD) before use as frying oils and phospholipids should have been substantially reduced in these processes. Results showed phosphorus content in WVO averaged 37 ppm with a standard deviation of 3 ppm. Because no oil samples were attained and tested for phosphorus content before frying, no concrete conclusions can be drawn as to where phosphorus was introduced into the WVO. However, it could have been the result of phosphorus transfer from food fried in the oils. The initial concentration of phosphorus in WVO, before frying and after commercially degumming (RBD), should have been much less than 10 ppm because phospholipids in transported oils can cause clogging and/or build-up issues in pipelines or tank walls, respectively.

4.7 Biodiesel Quality Experiment

4.7.1 Biodiesel Logic, Inc Biodiesel Processor

This experiment was designed as an addendum to Section 4.5 and therefore data presented in table 4.10 was compiled in the same manner as the methanol recovery experiment. As discussed in Chapter Three, proper mixing and interaction among WVO, methanol and sodium hydroxide was

theorized to be insufficient for the current configuration of this processor. The data in table 4.10 suggests that theory is plausible. Average mono-glyceride and di-glyceride values reported are fairly small but suggested complete transesterification of these constituents did not occur. Likewise, average tri-glyceride values were higher than mono-glyceride or di-glyceride values, indicating that on average, 2% to 3% of the mass of WVO was subjected to no transesterification.

ASTM Standard D 6751 (2007) requires total glycerin and free glycerin not exceed 0.24% mass and 0.02% mass, respectively. None of the treatments or resulting sample averages collected at various stages during the transesterification process met the requirement for total glycerin set forth by ASTM Standard D 6751. However, free glycerin requirements were met for samples collected after dry washing with AMBERLITE™ BD10DRY. This resin, as advertised by the manufacturer, should remove free glycerin among other constituents from biodiesel. This data supports manufacturer claims as free glycerin values were well below maximum limitations of ASTM Standard D 6751 (2007). Conversion efficiencies averaged around 96% and took into account mono-glyceride, di-glyceride and tri-glyceride values for each respective replication. Further, water content and FFA in WVO have the ability to inhibit complete transesterification. Therefore, samples of WVO from all samples were tested for water using ASTM Standard E 203-01 (2001) and FFA using ASTM Standard D 9555-95 (2008). Results concluded that water content in all sample averages was less than 0.2% suggesting no adverse effects on transesterification due to water content in the WVO. FFA values for all oil samples ranged from 1.9% to 2.3%.

Table 4.10. Quality of biodiesel produced from the Biodiesel Logic, Inc. processor.

Treatment*	Biodiesel sample	Conversion (wt%)		Total Glycerin (wt%)		Free Glycerin (wt%)		Mono-glycerides (wt%)		Di-glycerides (wt%)		Tri-glycerides (wt%)	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Standard	Raw biodiesel	97.38 a	1.42	0.38 a	0.20	0.07 ab	0.04	0.09 b	0.06	0.58 a	0.29	2.00 a	1.11
Vacuum		97.31 a	1.51	0.49 a	0.21	0.17 a	0.06	0.09 b	0.04	0.55 a	0.21	2.09 a	1.33
Standard	Post methanol recovery	97.47 a	1.24	0.32 a	0.24	0.09 ab	0.09	0.17 a	0.05	0.63 a	0.26	1.79 a	0.97
Vacuum		96.31 a	2.08	0.57 a	0.21	0.05 ab	0.04	0.12 ab	0.03	0.69 a	0.21	2.94 a	1.90
Standard	Post dry wash	95.63 a	2.73	0.51 a	0.31	0.00 b	0.00	0.06 b	0.02	0.95 a	0.45	3.41 a	2.30
Vacuum		96.02 a	0.88	0.47 a	0.10	0.01 b	0.01	0.07 b	0.03	0.77 a	0.23	3.20 a	0.81

Means assigned the same letter within columns are not significant ($P<0.05$).

*Treatments correspond to section 4.5.

4.7.2 Degummed Oils

There were three degumming methods selected for this experiment based on safety and practicality for a farmer. Table 4.9 highlights phosphorus concentrations in soybean biodiesel as a result of transesterification. As expected, phosphorus concentrations decreased. Greatest difference in phosphorus concentration was between soybean control oil and biodiesel. However, the phosphorus concentration of the soybean control biodiesel was not significantly different from other treatments. Degummed oil phosphorus concentrations were significantly different from the control treatment, but biodiesel phosphorus concentrations did not follow this trend. Although, hot water degummed soybean oil resulted in highest phosphorus concentration next to the control and biodiesel from this degummed soybean oil followed suit and exhibited highest phosphorus concentration. Likewise, anion resin degummed oil resulted in lowest phosphorus concentration as did biodiesel from anion resin degummed oil. Nonetheless, minimum ASTM D 6751 (2007) requirements for phosphorus concentration were not met. All mean phosphorus concentrations of biodiesel samples were between 22 ppm and 29 ppm. This may suggest that a threshold limitation existed in which transesterification removed phosphorus to a certain extent but was ineffective in removing phosphorus beyond that point.

Because some replications of canola oil did not transesterify, phosphorus results from the canola biodiesel data were not summarized but presented in table 4.11. Issues with transesterification of canola oil will be discussed further in this section, but anion exchange resin degummed canola biodiesel phosphorus concentrations were fairly consistent and lower than the mean of anion exchange resin degummed oil suggesting that some phosphorus was removed as a result of transesterification that was not removed during degumming alone. Other phosphorus content in biodiesel data was sporadic and inconsistent with the phosphorus value reported for citric acid degummed biodiesel higher than the mean of the degummed oil itself.

Table 4.11. Phosphorus content in degummed, transesterified canola oil.

Treatment	Rep	Mean phosphorus content in biodiesel (ppm)
Control	1	--
	2	45
	3	50
Citric acid	1	32
	2	--
	3	--
Hot water	1	--
	2	38
	3	39
Anion exchange resin	1	43
	2	43
	3	41

Data in table 4.12 partially summarizes results of soybean biodiesel quality from degummed vegetable oils tested in this experiment. FFA concentrations for soybean oil were consistent, on average, for degumming methods of citric acid and hot water, however, the average FFA concentration for the control and anion resin degummed samples were lower and significantly different from the previous two methods. Water was known to aid in hydrolysis of triglycerides, but FFA accumulation is typically experienced in the presence of heat as with frying oils. Lower average FFA concentration in the control sample was attributed to the fact that no water was introduced to the samples as in citric acid and hot water degummed oil samples. On the other hand, AMBERSEP™ BD 19 is advertised to remove cations, proteins and phospholipids. If FFA existed in the oil as a cation, the lesser value experienced, 0.20%, can be justified based on manufacturer performance specifications of the anion resin. Because samples in this experiment were produced on a micro scale and with 200 rpm agitation, adequate interaction among oil, methanol and sodium hydroxide are believed to have resulted in higher conversion efficiencies, 99.6% on average for soybean and WVO, than experienced in the methanol recovery biodiesel quality experiment. However, it is important to note that the molar ratio of alcohol to oil was 6:1 and 1 wt% sodium hydroxide was used in this experiment as opposed to 4.8:1 molar ratio of

methanol to oil and 0.7 wt% sodium hydroxide for the methanol recovery biodiesel quality experiment. The latter chemical amounts were recommended by the manufacturer of the Biodiesel Logic, Inc. biodiesel processer. Total glycerin concentrations in table 4.12 support the higher conversion efficiencies experienced and were considerably lower than those reported for the methanol recovery biodiesel quality experiment. Total glycerin average concentrations for each degumming method met requirement of ASTM Standard D 6751 (2007) of <0.24 wt.%. Likewise, mono-glyceride and di-glyceride values were very low as well. Tri-glyceride values were not even detected during GC analysis, further supporting extremely high conversion efficiencies and suggesting nearly complete transesterification of the respective vegetable oil. However, free glycerin values were high and did not meet ASTM Standard D 6751 (2007) requirements. This low level was attributed to the fact that the samples were not washed to remove free glycerin before analysis. This result further solidified the importance of washing biodiesel to remove free glycerin and other impurities in order to ensure quality.

WVO was also used as a control in this experiment both because it had previously been commercially refined before being used as frying oil and for comparison purposes to results obtained in Section 4.5. This oil was acquired from dining facilities just as the feedstock used in the methanol recovery biodiesel quality experiment. Even though FFA concentration was 2.3% on average, conversion efficiency was not inhibited and the oil performed similarly to soybean oil in terms of transesterification. This result provides further justification to the fact that agitation and interaction among constituents in the Biodiesel Logic, Inc. processor were inadequate.

Canola oil was also tested in this experiment under the exact conditions of soybean oil. It was mechanically extruded in the same time frame as soybean oil, stored in the same location and in containers of the same material. Also, both oils were stored for the same time interval, approximately eight months, before degumming and transesterification experiments ensued. However, results from canola oil were not as consistent as those obtained from soybean. In all degumming practices, except

with AMBERSEP™ BD19, at least one replication failed to transesterify and either solidified in the erlenmeyer flask or appeared unchanged as a result of transesterification. Although, when the oil appeared unchanged, half the amount of original methanol and sodium hydroxide could be added to the oil, the reaction performed again, and glycerol separation occurred. For this reason, averages were not calculated from this experiment and the data was reported unsummarized in table 4.13. However, important trends and findings can still be inferred from this data.

Of note were the extremely high FFA concentrations of all replications. Hydrolysis due to extended storage in non-air tight HDPE containers was attributed to excessive hydrolysis; however, hydrolysis in soybean oil was substantially less than canola. For canola oil, just as in soybean, AMBERSEP™ BD19 consistently lowered FFA values and all replications of canola oil degummed with AMBERSEP™ BD19 transesterified with excellent quality results. Although FFA values were three times higher than researcher recommended base catalyzed transesterification ceiling limits, samples that did transesterify resulted in nearly complete conversion with exception to replication three of the canola control oil in which only 62% of triglycerides converted to fatty acid methyl esters.

The exact reason canola oil replications did not consistently transesterify is unknown. However, once this problem was realized, measures were taken to attempt to answer this question. Samples collected from the storage container to be used in the degumming and transesterification experiments were collected from near the bottom of the container. Therefore, oil stratification was considered as a culprit of inconsistency in the data. It is speculated that proteins, gums and other impurities with greater density than oil moved towards the bottom of the storage container due to gravity (Burkhalter, 1976) and may have resulted in transesterification failure of the canola oil. Thereby, 10, 95-g canola oil samples were collected from the remaining oil stored in the bottom of the original canola oil storage container. Likewise, 10, 95-g canola oil samples were collected from another bucket of the exact same oil, mechanically extruded at the same time and stored in the same container type and for the same

time duration. However, oil in this bucket had not yet been used for experimental analysis and the samples were drawn from the top layer of oil. FFA concentration was tested for each oil sample from both buckets with an average of 6.62% for samples drawn from the bottom of the storage container and 6.24% for samples collected from the top layer of the other storage container of canola oil. Transesterification procedures were conducted on these 20 samples just as in previous micro-scale transesterification experiments. All 10 samples from the top layer of the second canola oil storage container consistently transesterified. However, the 10 samples drawn from the bottom layer of the first canola oil storage container failed to transesterify. Although there was a minor difference in FFA concentration, transesterification failure may suggest that oil stratification occurred in the canola oil rendering the lower layer unusable for biodiesel production.

Table 4.12 Quality of biodiesel produced from degummed vegetable oils (soybean and WVO).

		Oil FFA (%)		Conversion (wt%)		Total Glycerin (wt%)		Free Glycerin (wt%)		Mono-glyceride (wt%)		Di-glyceride (wt%)		Tri-glyceride (wt%)	
Oil	**Treatment**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
Soybean	Citric acid	0.38 a	0.00	99.84 a	0.03	0.06 a	0.07	0.68 a	1.07	0.07 a	0.06	0.05 a	0.01	0.00 a	0.00
	Hot water	0.38 a	0.00	99.88 a	0.09	0.07 a	0.08	0.78 a	1.19	0.06 a	0.05	0.06 a	0.00	0.00 a	0.00
	AMBERSEP ™ BD19	0.20 b	0.04	99.88 a	0.01	0.10 a	0.11	1.32 a	1.56	0.08 a	0.01	0.03 b	0.01	0.00 a	0.00
	Control	0.26 b	0.04	99.87 a	0.00	0.06 a	0.08	0.71 a	1.18	0.01 a	0.00	0.05 b	0.00	0.00 a	0.00
WVO	Control	2.32	0.09	99.87	0.01	0.01	0.00	0.03	0.00	0.04	0.00	0.05	0.01	0.00	0.00

Means assigned the same letter within a column are not significant (P<0.05).
WVO not included in statistical analysis of soybean biodiesel quality.

Table 4.13. Quality of biodiesel produced from degummed vegetable oils (canola).

			Conversion (wt%)		Total Glycerin (wt%)		Free Glycerin (wt%)		Mono-glyceride (wt%)		Di-glyceride (wt%)		Tri-glyceride (wt%)	
Treatment	**Rep**	**Oil FFA (%)**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
Citric acid	1	6.59	99.88	0.00	0.03	0.00	0.23	0.04	0.08	0.02	0.02	0.01	0.01	0.00
	2	6.67	--	--	--	--	--	--	--	--	--	--	--	--
	3	7.20	--	--	--	--	--	--	--	--	--	--	--	--
Hot water	1	6.59	--	--	--	--	--	--	--	--	--	--	--	--
	2	6.67	99.54	0.00	0.07	0.00	0.27	0.06	0.11	0.00	0.07	0.00	0.17	0.02
	3	6.74	99.84	0.07	0.06	0.07	0.72	0.99	0.09	0.00	0.03	0.00	0.03	0.01
AMBERSEP™ BD19	1	5.13	98.44	0.02	0.24	0.02	0.95	0.17	0.15	0.00	0.15	0.01	0.75	0.04
	2	5.52	98.07	0.07	0.37	0.06	2.29	0.96	0.15	0.00	0.19	0.00	0.95	0.02
	3	5.59	99.10	0.02	0.01	0.00	0.05	0.01	0.01	0.00	0.01	0.00	0.04	0.00
Control	1	6.51	--	--	--	--	--	--	--	--	--	--	--	--
	2	6.82	95.57	0.05	0.70	0.04	2.82	0.04	0.08	0.01	0.51	0.04	2.18	0.18
	3	6.51	61.77	0.01	4.95	0.01	2.20	0.21	4.83	0.51	4.21	0.24	18.07	0.04

*Data not included in this table is the result of sample failure during transesterification.

4.8 Mechanical Extruder Efficiency Analysis

Mean mechanical screw press assessment data is outlined in table 4.14. The Henan Double Elephant mechanical screw press (1) was evaluated with three different oilseeds and soybean resulted in highest oil extraction efficiency. That is, the highest percentage of oil relative to total seed oil was extracted from soybean. Mechanical screw presses have been estimated to be capable of extracting up to 80 – 85% of the total seed oil, thus results for soybean are favorable. However, sunflower and canola results were considerably lower in terms of oil extraction efficiency. Several factors were attributed to the lower results observed. For the Henan Double Elephant press, operator aptitude heavily dictates oil output. There are several movable components of this press that adjust position of the screw and spacing between the plates. Figure 4.11 shows an operator positioning the screw. These parts must be loosened to begin processing and when the mechanical screw press warms up, the parts are tightened to optimal operating conditions as perceived by the operator. Of course, these parameters are specific for different oilseeds and may be based on several factors (e.g. particle size, density and moisture content).

Table 4.14. Henan Double Elephant model 6YL-120 (1) and Karl Strähle SK60/2 (2) mechanical screw press assessment summary.

Mechanical Screw Press	Oilseed	Moisture Content (%w.b.)*	Oilseed input (kg/hr)	Oil output (L/hr)	Oilseeds in/oil out (kg/L)	Oil Extraction Efficiency (%)
1	Sunflower	NA	67.3	17.9	3.8	48.4
	Soybean	12.6	109.2	15.7	7.0	77.3
	Canola	6.9	150.4	22.4	6.7	34.1
2	Canola	6.8	47.8	10.2	4.7	48.5

* w.b. denotes wet basis.
Sunflower moisture content was not available (NA).

On the other hand, the Karl Strähle mechanical screw press has fixed components and requires minimal user knowledge. Oilseeds are slowly fed into the press to bring it up to operating temperature,

and then the oilseed can be freely fed into the press from the hopper bag figure 4.12. This machine has a dual augering system and both sides can be used simultaneously. Augers for this press are oilseed specific and it is possible to press two different oilseed types simultaneously. In table 4.14, canola was the only oilseed type reported. If comparisons are made for extraction efficiencies for canola between the two mechanical screw presses, the Karl Strähle press outperforms the Henan Double Elephant by approximately 41%. Again, it is speculated that the increased extraction efficiency is due to operational parameters. At some level and with hours of experience, extraction efficiencies of a devoted operator on the Henan Double Elephant may exceed those of the Karl Strähle. However, it is not known how long this learning curve might take and still how much valuable oil might be lost in the process.

Figure 4.11. Operator adjusting screw position on a Henan Double Elephant 6YL-120 mechanical screw press for optimal oil output.

Another advantage that the Karl Strahle press holds over the Henan Double Elephant is operator efficiency. During testing and after machine warm-up, the only operator input was to empty oil and cake catchment containers and refill the hopper. The Henan Double Elephant required the manufacturing of a separate hopper and auger system that continually fed the press (figure 4.13).

Figure 4.12. Karl Strahle SK60/2 mechanical screw press.

Figure 4.13. Hopper and augering system designed and built for the Henan Double Elephant mechanical screw press.

4.9 Economic Analysis of Small-scale Biodiesel Production Systems

4.9.1 Auburn University's Biosystems Engineering Biodiesel Production System

Table 4.15 reports the economic analysis of Auburn University's Biosystems engineering biodiesel production system on a yearly basis. For this analysis, collection site equipment at the dining facilities on Auburn's campus cost $145 annually. This equipment was a requirement by the university and would not necessarily be required if this exact system were implemented on-farm. Likewise, partial costs of other equipment such as storage equipment and spill containment, would likely not be incurred for an on-farm setup. The storage equipment cost for this analysis was calculated from list prices for new storage tanks, however Biosystems Engineering staff were able to acquire the storage tanks for less than the analysis reports. For this reason, it was suspected that a farmer could likely acquire necessary items in a similar manner, lowering the overall cost/volume of the biodiesel.

The economic analysis also illustrated that the highest annual cost was incurred for the biodiesel processor. The processor was purchased by Auburn University for $17,000 with an educator's discount. A 10-year straight-line depreciation was used for this analysis, but it is likely that, if properly maintained, the biodiesel processor could easily last beyond 10 years. A longer life would decrease production cost. Labor was the second highest cost of the analysis and was calculated using hourly labor cost published by ACES (2011). Again, labor costs could vary from farm-to-farm and cause minor fluctuation in overall cost per gallon of biodiesel production. Transportation cost was estimated using approximate mileage traveled while collecting WVO and the standard mileage rate charged for Auburn University vehicles. Nevertheless for Auburn University's Biosystems engineering biodiesel production system, it was estimated that biodiesel is produced annually at a cost of $2.21 per gallon ($0.58/L). At the writing of this thesis, Alabama Cooperative Extension System Profit Profiles reported that current Alabama farm diesel fuel prices range from $3.29 to $3.52 per gallon for quantities purchased greater than 1000

gallons (ACES, 2011). If Auburn University's current biodiesel production system was implemented on-farm at the current annual production rate of 3,300 gallons per year, the production cost of $2.21 per gallon would currently save farmers on average $1.21 per gallon and the current total biodiesel volume produced would save farmers almost $4,000 for the year. Approximately 2.7 gallons of methanol is currently lost when glycerol is drained from the reactor. If this methanol were recovered for recycling in addition to methanol recovered from the raw biodiesel, approximately $385 per year would be saved bringing the yearly savings to almost $4,400 by using biodiesel as opposed to petroleum diesel.

Table 4.15. Annual economic analysis for Auburn University's Biosystems Engineering biodiesel production system.

	Estimate
Collection Site Equipment	$144
Biodiesel Production Equipment	
Storage Equipment	$485
Biodiesel Processor	$2,531
Processing Chemicals & Related Items	$1,498
Spill Containment & Clean-up Items	$210
Transportation cost	$943
Operating Costs	
Labor	$1,450
Power	$27
WVO collected (gal)	3,300
Total Yearly Cost	$7,289
Cost per gallon	$2.21

*Calculated with straight-line depreciation
†All costs are USD

4.9.2 Small-scale, On-farm Biodiesel Production System

An economic model was developed for a small-scale, on-farm biodiesel production scenario (Table. 4.16) based on Section 4.9.1. Biodiesel production costs were used with oilseed processing costs

and commodity prices (opportunity costs) factored in as well. Some costs of spill containment and collection site equipment were omitted because they were requirements of Auburn University's Risk Management division and were not a requirement of the on-farm set-up. Oilseed yields were taken from mean experimental yields for 2008-2010 from Section 4.2. Oilseed cake generated from mechanically pressed oilseeds was given a weight basis value equivalent to soyhull pellets, as was assumed to be fed to livestock and partially replace the need to purchase soyhull pellets.

The *Input* section of the model was designed to be used by a farmer so that they could enter actual values from his operation. They would start by entering production acres of soybean and/or canola that he intended to use for biodiesel production followed by a yearly volume of WVO that he planned to collect and process. Next, he or she would enter anticipated crop yields that should be based on yield history. Commodity prices are entered next. While prices are highly variable, contract or future commodity prices will provide a market value. Finally, they would input the value of soyhull pellets. From these parameters, estimates will be generated for total biodiesel yield, meal produced, commodity price, and meal value. If WVO is a factor of the model for the year, transportation cost for acquiring the WVO will be estimated as well.

A subsection of the model will also recommend needed equipment for the biodiesel operation. The *Recommended equipment* subsection (table 4.17) includes suggestions for processor capacity based on commercially available biodiesel processors offered by Biodiesel Logic, Inc., an estimate of batches produced per week based on oilseed production area and volume of WVO entered, an estimate of oil storage containers needed per two week time period, drums needed for storing the glycerol co-product of transesterification, and AMBERLITE™ BD10Dry needed per year. Assumptions were made that no more than four batches of biodiesel would be made per week, oil needed two weeks for particulates to settle, and glycerol would be disposed of or fed to livestock within two weeks.

Table 4.16. Annual economic model for small-scale, on-farm biodiesel production.

	Input
Oilseed Production (ac)	
Soybean	50
Canola	200
Waste Vegetable Oil (WVO) (gal)	2,000
Oilseed Yield (bu/ac)	
Soybean	52.26
Canola	35.42
Commodity Price ($/bu)	
Soybean	$13.70
Canola	$13.31
Soyhull pellets ($/ton)	$180
	Model
Estimated Biodiesel Produced (gal)	
Soybean	2,826
Canola	15,301
WVO	2,000
Estimated Meal Produced (ton)	
Soybean	68
Canola	120
Estimated Total Commodity Value ($)	
Soybean	$35,798
Canola	$94,288
Estimated Total Meal Value ($)	
Soybean	$12,203
Canola	$21,550
Estimated WVO Transportation Cost ($)	$580
Oilseed Extrusion	
Mechanical Screw Press	$1,200
Biodiesel Production	
Storage Equipment	$328
Biodiesel Processor	$6,186
Processing Chemicals & Related Items	$9,010
Spill Containment & Clean-up Items	$143
Operating Costs	
Labor	$15,483
Power	$202
Total Biodiesel Produced (gal)	20,128
Total Yearly Cost	$129,465
Cost per gallon	$6.43

*Calculated with straight-line depreciation
†All costs are USD

Table 4.17 Small-scale, on-farm biodiesel production system recommended equipment.

Recommended equipment	Estimate
Processor capacity (gal)*	275
biodiesel batches processed per week†	2
275-gal oil storage totes	3
55-gal drums for glycerol collection	3
AMBERLITE™ BD10Dry needed per year	2

*Biodiesel processor based on commercially available models from Biodiesel Logic, Inc.
†Based on maximum of four batches per week.

Fixed costs of the mechanical screw press, biodiesel processor, and associated equipment were assigned a life expectancy and straight-line depreciation was used to determine annual costs. Processing chemicals were given 2010 values and labor cost was calculated based on quantity of oilseeds to process, biodiesel batches to produce, and an estimated farm laborer wage (ACES, 2011). Power cost was projected based on kilowatt hours required by the mechanical screw press and biodiesel processor to process estimated oilseeds and biodiesel batches. Highest costs were determined for commodity opportunity cost, processing chemical costs, and labor.

Figures 4.14, 4.15, and 4.16 illustrate biodiesel production costs per volume. Soybean and canola biodiesel production costs were determined on an acreage basis and highlighted fluctuations of biodiesel production costs for the past year based on commodity market trends. Biodiesel produced from soybeans showed highest production costs and was attributed to higher commodity prices. Economy of scale was favorable for this model in that an increase in production acres lowered the overall production cost of biodiesel on a volume basis. WVO utilized for biodiesel resulted in lowest production cost as compared to soybean and canola. This was attributed to the fact that WVO was assumed to essentially be a free feedstock and the only cost associated with WVO was transportation. Increasing volumes of WVO lowered the overall cost of production; 5,000 gallons was estimated to cost $1.40/gal. Lowest production costs for soybeans and canola were experienced for monthly commodity

prices of April, 2010 and with 500 acres of production. They were determined to be $6.81/gal and $4.07/gal, respectively.

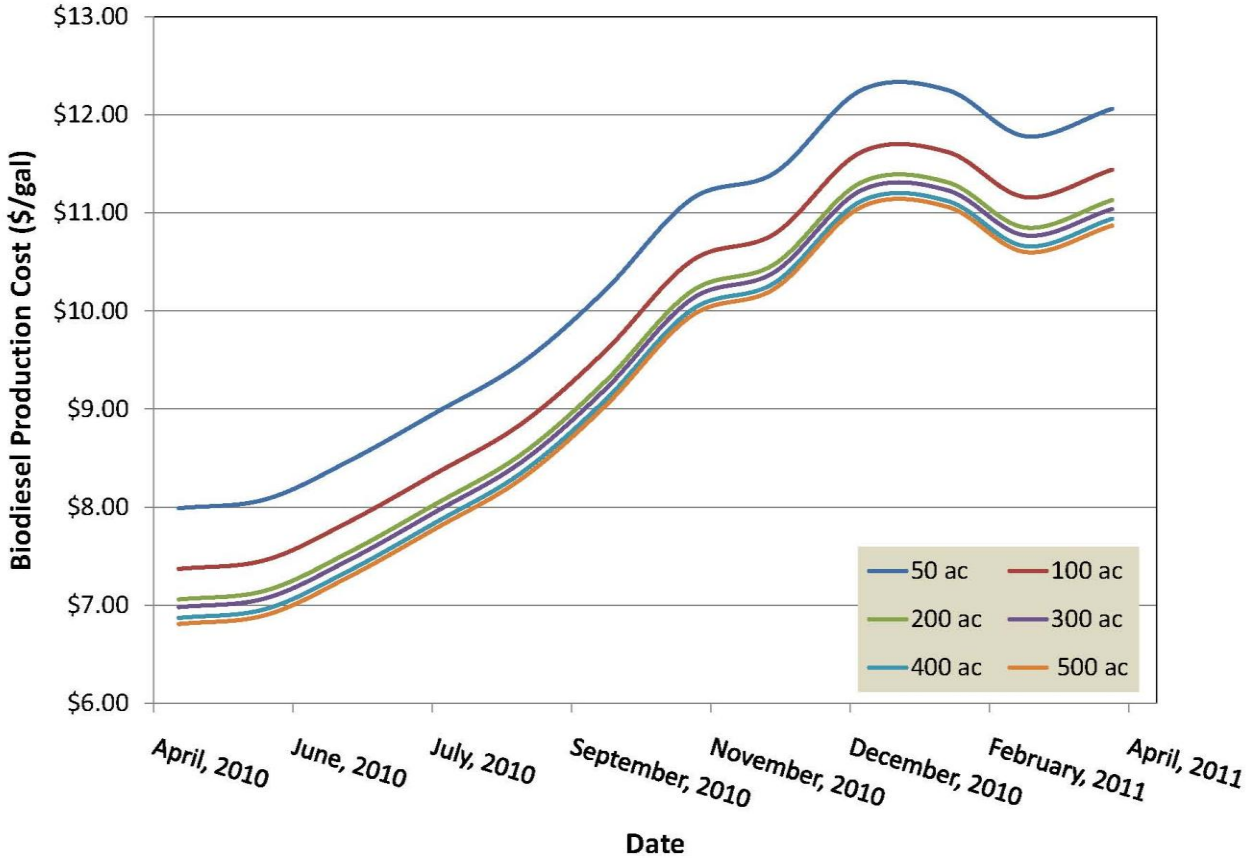

Figure 4.14. Soybean biodiesel production cost based on historical commodity prices and production area.

Table 4.17 provides economic profits or losses for soybean producers in Alabama from 2006 to 2010 (ACES, 2010). An average loss of $101.22/acre was experienced by soybean producers in 2010 when selling crops through traditional commodity markets. When this profit/loss data was entered into the model with production acreage of 500 acres, a loss of $91.22/acre was calculated. If in 2010, a farmer produced biodiesel with 500 acres of soybeans as opposed to selling them through traditional commodity markets, they would have decreased his net losses by $10.00/ac. Figure 4.17 showed that the breakeven losses were at a soybean price of approximately $11.40/bu meaning that for 2010, a farmer would have had an economic advantage by producing biodiesel when soybean prices were below

$11.40/bu. If soybean prices had risen above $11.40/bu, they would have benefitted most by selling the crop through commodity markets. However, for soybean prices below $15.09/bu, he or she would have still suffered a loss.

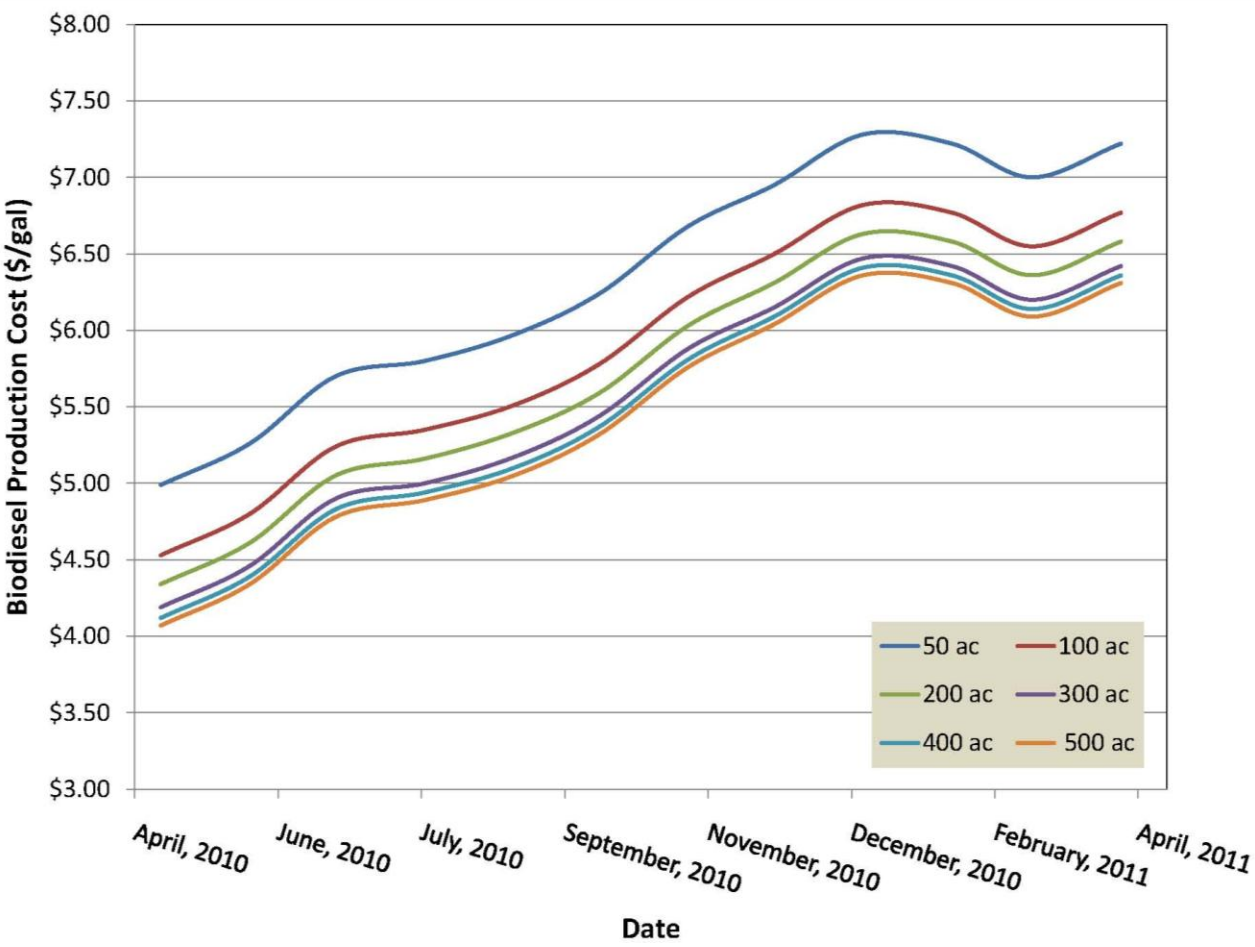

Figure 4.15. Canola biodiesel production cost based on historical commodity prices and production area.

In order for small-scale, on-farm biodiesel production to be economical, net losses must be less when retaining the oilseeds on farm and producing biodiesel than when selling crops through traditional commodity markets. In 2010, an average reduction in losses of $10.00/ac could have been experienced with small-scale, on-farm biodiesel production. Although, the profit/loss estimates in table 4.18 illustrate how volatile commodity markets have been over the past five years. From this data, it is evident that loss reductions or profits will vary substantially from year-to-year. However, Paulson and

Ginder (2007) and Kenkel and Holcomb (2006) alluded to the fact that one aspect of recent oilseed market volatility may have been brought about by increased interest in biodiesel production. By keeping oilseeds grown for biodiesel production on-farm, they never enter the commodity market. If small-scale, on-farm biodiesel production systems were widely accepted and practiced and portions of crops were not sold through trading venues, markets may eventually stabilize.

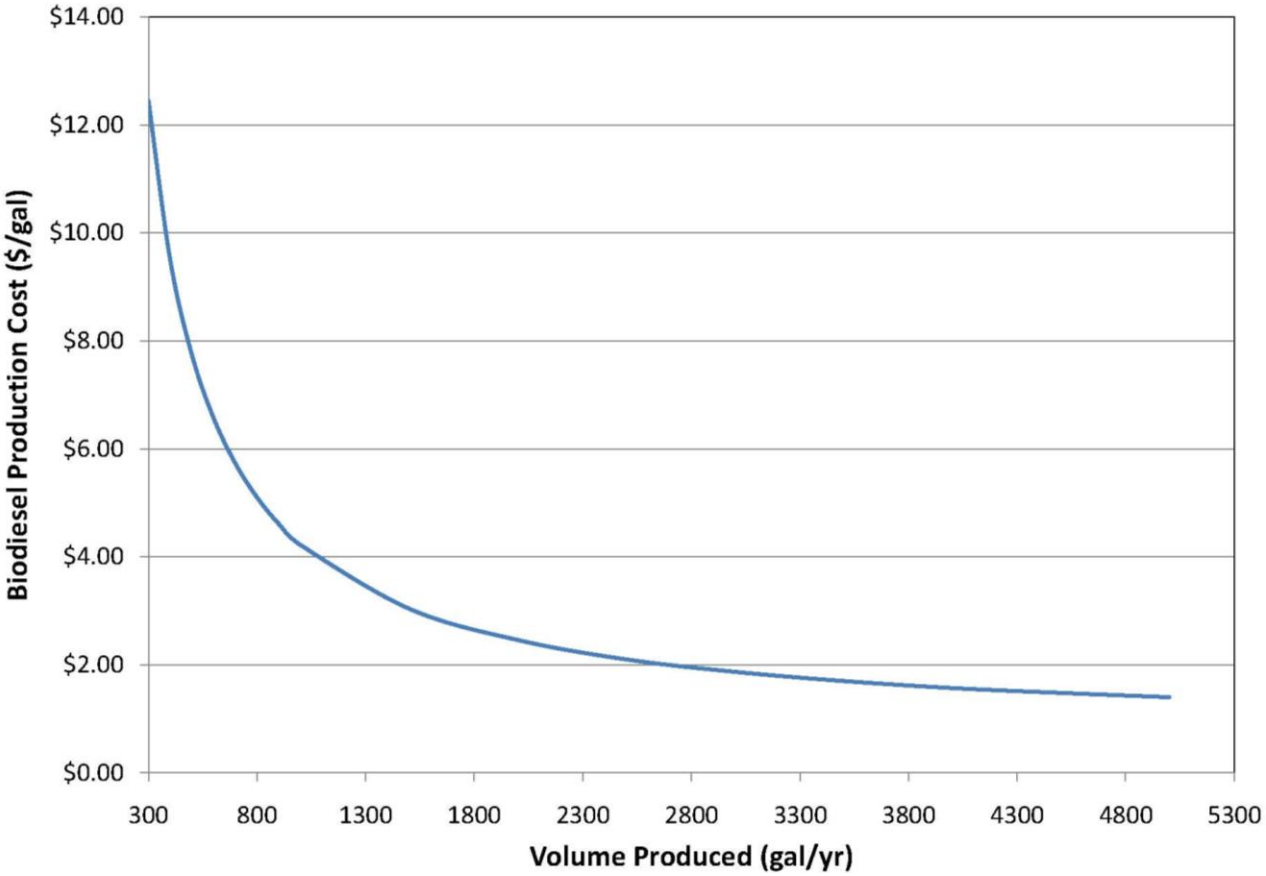

Figure 4.16. WVO biodiesel production cost.

Table 4.18. 2006-2010 Soybean Profit/Loss Economics (ACES, 2011).

Year	Mean cost of production/ac	Mean yield (bu/ac)	Mean price ($/bu)	Profit/Loss ($/ac)
2006	238.73	20	6.85	-110.73
2007	262.51	21	11.40	-23.11
2008	309.76	35	10.30	50.74
2009	394.38	40	10.40	21.62
2010	392.42	26	11.20	-101.22

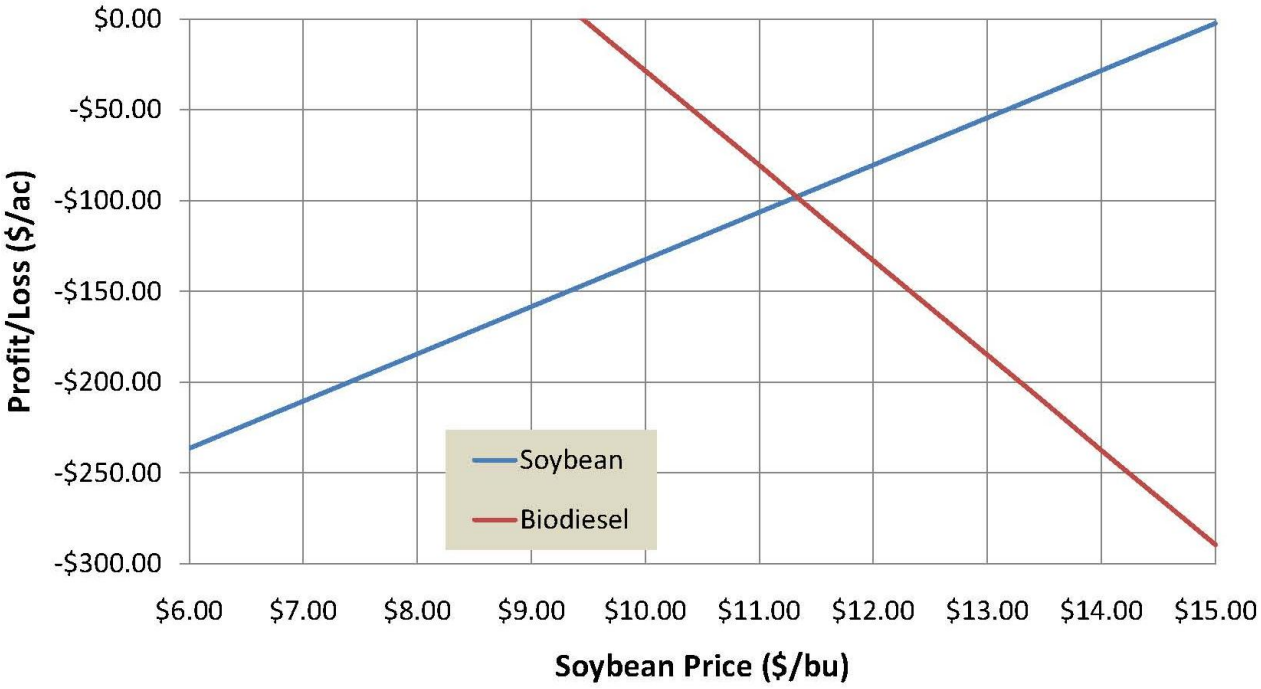

Figure 4.17. 2010 soybean commodity value vs. biodiesel production profit/loss breakeven point.

The feasibility of small-scale biodiesel production at the farm level was justifiable in Alabama from 2010 soybean economic data alone. Because canola is not a frequently grown crop in the state, no profit/loss data was available. However, considering that canola contains twice the oil content of soybean, but is grown as a winter crop with fewer required inputs, biodiesel yield would be higher but cost of crop production would be lower, respectively. Thus, the breakeven point would be somewhat different from soybeans. Nonetheless, cost of biodiesel production from canola was $2.50/gal to $3.00/gal cheaper than soybean biodiesel. Reduced production cost, coupled with a winter growing season, make canola appealing for Alabama farmers who wish to supplement their fuel needs with biodiesel. If WVO was added to on-farm biodiesel feedstock, cost of production would be further reduced and even has the potential to approach current petroleum fuel prices.

To investigate the response of biodiesel cost of production to reductions in model parameters, a simple sensitivity analysis was conducted (table 4.19). Four of the highest costs within the model were reduced from 5% to 50% with cost of production calculated for each individually. Then, a collective cost

of production was calculated for all four parameters at the respective percent reduction. This analysis revealed that a cost reduction of just above 30% for the four parameters would result in biodiesel cost of production equaling current farm petroleum diesel fuel prices reported by ACES. Major reductions in cost of production were attributed largely to commodity price reduction. While reduction in commodity prices by 30% is not likely, labor and processor cost reductions may be feasible for Alabama farmers. Reduction of labor cost could be accomplished by increasing automation and efficiency of oil extraction from oilseeds. Processor cost could be reduced if a farmer designed and fabricated his or her own. These reductions could easily range from 30% to 50% or higher for a mechanically inclined farmer. However, labor and processor cost were not found to be major cost reducing parameters in lowering cost of production of biodiesel.

Table 4.19. Biodiesel cost of production sensitivity analysis.

Reduction in Cost (%)	-------Cost of Production ($/gal)-------				Collective Cost of Production ($/gal)
	Labor	Processor	Canola	Soybeans	
5%	$6.39	$6.42	$6.14	$6.31	$5.97
10%	$6.36	$6.40	$5.86	$6.19	$5.51
20%	$6.28	$6.37	$5.28	$5.96	$4.59
30%	$6.20	$6.34	$4.71	$5.72	$3.67
40%	$6.12	$6.31	$4.13	$5.48	$2.75
50%	$6.05	$6.28	$3.55	$5.24	$1.82

CHAPTER FIVE
SUMMARY AND CONCLUSIONS

5.1 Summary

The goal of this research was to facilitate understanding of an integrated small-scale, on-farm biodiesel production system and potential of minimizing variability associated with oilseed production and processing, biodiesel quality and volatile farm input costs for an Alabama farm. The experiments performed, data collected, and analysis of results suggested that farmers could have reduced 2010 profit losses by $24.70/ha, on average by implementing this system.

A non-traditional bioenergy crop rotation experiment was initiated and crop constituent responses (i.e. oil, protein, and oil FFA) to varying levels of irrigation were assessed in the first experiment. Results indicated that over the course of the three years of the study, soybean and cotton yields significantly improved as a result of increasing levels of irrigation. Most notable results were experienced in 2010 when total seasonal rainfall was 13.4 cm and responses to irrigation accounted for 380% and 166% increases in theoretical biodiesel yield in soybeans and cotton, respectively. Canola was grown as a winter crop with no irrigation applied after emergence and although the experiment was too new to determine rotational effects, 2010 theoretical biodiesel yield was 200% higher than 2008 due to an additional 17 cm of rainfall received during the growing season.

Oil concentrations of the three crops varied 2% to 3% with experimental averages of 19%, 44% and 22% for soybeans, canola and cotton, respectively reported on a dry matter basis. Slight trends existed in which oil concentration increased with increasing irrigation. This result favors well with crop yield responses to irrigation because the major limiting factor of theoretical biodiesel output was

determined to be crop yield. Increased yield and oil output as a product of increasing irrigation will further accentuate theoretical biodiesel yield. However, protein concentration showed slight trends to decrease with increasing irrigation levels and differed by an average of 20% among the three crops with highest protein concentrations found in soybean of approximately 36%.

In most oilseed crop experiments, FFA levels remained below one percent which was complimentary for biodiesel production. However, in 2009 FFA concentrations in cottonseed were 20 times higher, averaging 9% among irrigation treatments. Elevated FFA was attributed to excessive end of the season rainfall and prolonged seed exposure to moisture after the bolls opened. Harvest was delayed due to wet field conditions with seeds beginning to germinate and oils undergoing hydrolysis. Oilseeds subjected to these conditions will not be suitable for biodiesel production and should be sold through traditional commodity markets or, in the case of cottonseeds, traded in return for cotton ginning.

The biodiesel production procedure literature review revealed base catalyzed transesterification to be the least expensive and safest method of producing biodiesel. Methanol at an alcohol to oil molar ratio of 6:1, 1 wt.% sodium hydroxide, reaction time of four hours and reaction temperature of 60 ^{o}C resulted in >96% ester conversion at a chemical cost of $0.16/L. However, very similar results were obtained at reaction duration of one hour. Similarly, oil types of soybean, sunflower, peanut, canola, and cottonseed were reviewed in published literature with base catalyzed transesterification procedures comparable to the one stated above yielding >95% ester conversion.

Canola, soybean and WVO stored in HDPE containers over an approximate nine month period resulted in varying triglyceride hydrolysis rates but no noticeable microbial activity. WVO and canola oxidized 68% and 43% with FFA levels reaching 4.7% and 3.3%, respectively. On the other hand, soybean oil oxidized 50% but resulted in only 0.3% FFA. After nine months of storage in a sealed HDPE container,

soybean oil was be most favorable for base catalyzed biodiesel production in terms of FFA. WVO and canola oil may be transesterified, but an acid pretreatment may be necessary for optimal ester yield.

Absorbance data from soybean, canola, and WVO oils resulted in similar mean readings over time as control samples. Optical density of the samples over time, while a relative measurement, showed no increases at the 550-nm wavelength indicating no microbial activity. Unlike experimental samples, bacteria positive control samples revealed substantial absorbance increase at 550-nm wavelength with optical density readings increasing with each incremental increase of bacteria concentration.

Methanol recovery efficiency in the Biodiesel Logic, Inc processor was increased by 600% with assistance of a vacuum pump. Average savings of $1.28 per 90-L batch were found when using the vacuum pump and residual methanol in biodiesel was decreased from 3.04 L to 0.8 L. This reduction in residual methanol not only makes the end product safer to handle, store and transport, but also recovers sufficient methanol for future use to compensate for power requirements of upcoming batches.

Phosphorus removal from vegetable oils was greatest with the citric acid method in canola oil and anion exchange resin in soybean oil. Control samples of canola oil and soybean oil contained 51 ppm and 45 ppm and phosphorus levels were reduced to 26 ppm and 24 ppm, respectively. Even after transesterification of the degummed oils, soybean biodiesel from the anion exchange degumming treatment resulted in 22 ppm phosphorus, which was the experimentally lowest level reached. However, ASTM Standard D 6751 (2007) requires no more than 10 ppm phosphorus and none of the degumming treatments or biodiesel produced from the degummed oil achieved this level.

Biodiesel quality from the Biodiesel Logic, Inc. biodiesel processor resulted in an average 96.7% ester conversion. This conversion efficiency was better than expected considering oil/methanol interaction was poor due to no active mixing within the reactor vessel. Mean free glycerin was reduced

in each contiguous sampling. This result indicated that some post transesterification reaction took place during methanol recovery, but almost all free glycerin was removed during dry washing. The AMBERLITE™ BD10Dry resin used to refine the biodiesel worked well with ASTM Standard D 6751 (2007) being met in terms of free glycerin requirements. When comparing biodiesel quality from this experiment to biodiesel produced on a bench scale from degummed soybean and canola oils, ester conversions were significantly higher on average for the bench scale experiment (99.5%). The ester conversion result from the bench scale experiment further solidified the fact that poor methanol/oil interaction was experienced in the Biodiesel Logic, Inc. processor. However, not all samples of canola oil successfully transesterified from the degumming experiment. Anion exchange resin degummed samples of canola oil transesterified successfully. The resin manufacturer stated that the resin was effective in removing proteins, phospholipids and cations. FFA concentrations were high with proteins and cations attributed to transesterification failure in non anion resin degummed samples.

Oil extraction efficiency varied from crop-to-crop with the Henan Double Elephant mechanical screw press. Operator aptitude is crucial with this press as it has several movable components that must be optimized to maximize oil output. An extraction efficiency of 77% was achieved with soybeans, however other oilseeds of sunflower and canola resulted in only 48% and 34% extraction efficiency, respectively. The Karl Strähle mechanical screw press resulted in 49% oil extraction efficiency which was 144% higher than the Henan Double Elephant press. This increase in oil output was attributed to the fact that the Karl Strähle press contained fixed parts with less of an operator learning curve.

Economic analysis of Auburn University's Biosystems Engineering small-scale biodiesel production system revealed an annual WVO processing volume of 3,300 gal. Parameters of transportation cost, equipment, labor and power requirements were assessed and a yearly production cost of $2.21/gal was determined. The data from this system was extrapolated to a small-scale on-farm biodiesel production system scenario and a prediction model developed. It was determined that

soybean resulted in the highest production cost, followed by canola and WVO, respectively. Increased production cost was attributed to higher commodity prices and differences in oil concentrations between crops. WVO was assumed to be a free feedstock with the only associated cost of the oil being transportation. Even though soybean resulted in highest biodiesel production cost, an economic gain of $10.00/ac resulted from producing biodiesel with soybeans grown on-farm as opposed to selling them through traditional commodity venues. An average acreage loss of $101.22 was experienced by Alabama soybean producers in 2010, but only $91.22/ac loss would have been experienced if the soybean crop had been used for biodiesel production. No tax credits or subsidies were taken into account in this scenario.

From this study, we learned that irrigation improved theoretical biodiesel yield in oilseed crops by increasing overall crop yields. Seasonal rainfall influenced crop yields as well and irrigation was most valuable in years of limited precipitation. Simple methods of degumming crude vegetable oil were not effective in meeting ASTM requirements, but satisfactory biodiesel conversion efficiencies were obtained with proper oil/methanol interaction. Vacuum pump assistance during methanol recovery was imperative to achieve maximum return and a safe end product. In conclusion, a small-scale, on-farm biodiesel production system can provide quality biodiesel at an economic advantage, especially during periods of market volatility as experienced in recent years and while supplementing both on-farm fuel and livestock feed requirements. But most importantly, this system provides Alabama farmers a viable alternative to selling crops through traditional commodity venues in order to maximize returns and allows them the option of deciding the most beneficial means of crop utilization during periods of uncertainty.

5.2 General Conclusions

The conclusions of this research are as follows:

1) Oilseed constituents were impacted by varying levels of irrigation. In terms of biodiesel production, which was the focus of this study, oilseed yield was the limiting factor for biodiesel output and soybean and cotton crops responded positively to increasing levels of irrigation. The 125% pan evaporation treatment adjusted for percent crop canopy resulted in highest yield in years when rainfall was limited. Because canola was grown as a winter crop, irrigation was only applied through emergence. However, increased rainfall during the canola growing season significantly increased yield, which in turn increased theoretical biodiesel output. Similarly, oil concentration was increased with increasing irrigation and closely paralleled yield responses, thus resulting favorably to biodiesel output. Protein showed a slight negative trend with increasing irrigation, but overall FFA was not affected at a substantial level by irrigation to effect biodiesel output. However, in years when excessive end of season rainfall is experienced, care should be taken when considering utilizing oilseed crops grown for biodiesel production. FFA levels unsuitable for base catalyzed transesterification were experienced as a result of high moisture coupled with late harvest. When this scenario is experienced, selling crops through traditional commodity markets would be strongly advised.

2) A base catalyzed transesterification procedure using a 6:1 molar ratio of methanol to oil, 1 wt.% sodium hydroxide, reaction time and temperature of one hour and 60 ^{o}C was recommended based on production procedure literature review and cost of biodiesel production associated with this method. According to published literature, this method resulted in satisfactory biodiesel quality at least chemical expense. While phosphorus removal procedures were simplistic and safe for an on-farm system, ASTM requirements were not met. However, to ensure consistent, quality transesterification results of stored vegetable oils, especially canola oil, AMBERSEP™ BD19 may be used. Degumming before storage is recommended as this has the potential to increase phosphorus removal efficiency. In terms of storage,

oils should be stored in air-tight containers, out of sunlight and in cool temperatures to minimize hydrolysis. If stored properly, soybean oil will be easily transesterified after a nine month storage interval. Canola oil and WVO stored in proper conditions for nine months may effectively convert to biodiesel, but bench scale transesterification tests are recommended, prior to batch reactions, to determine whether a batch reaction will satisfactorily convert. If crude oils are stored long-term without first degumming, the bottom portion of oil should not be used for biodiesel production without a bench scale test to ensure conversion.

3) Small-scale, on-farm biodiesel production can be feasible, even economical during years of farm input market volatility. A system such as this not only minimizes potential profit losses during market fluctuations, but also provides security for the future of the operation. Fuel and livestock feed requirements can be effectively supplemented and farmers have a feasible alternative to selling crops through traditional markets when economics are favorable. Biodiesel production from soybeans resulted in higher production cost due to elevated commodity price. However, a biodiesel production system where more canola is utilized as opposed to soybeans and along with WVO, production costs will begin to approach current petroleum fuel prices. Further, canola will be grown as a winter crop and not impact potential profits of crops grown during the conventional cropping season.

5.3 Future Research

Crude vegetable oil degumming experiments were ineffective in meeting ASTM threshold requirements for phosphorus. However, citric acid showed the most promise in canola oil. Future research should include experimentation with varying concentrations of an aqueous citric acid solution to determine if phosphorus requirements can be obtained. Likewise, canola oil was complicated to transesterify after approximately eight months of storage. Gums and proteins were attributed to transesterification difficulty and oil stratification was suspected as well. Future research should focus on

determining the magnitude of oil stratification, if degumming practices prior to storage can minimize stratification, and quantify proteins and cations removed from canola oil when using AMBERSEP™ BD19. These research strategies are expected to increase consistency in canola oil transesterification.

Poor methanol/oil interaction was determined in the Biodiesel Logic, Inc. processor. This poor interaction was believed to be the cause of lower conversion efficiencies as compared to bench scale reactions. Implementation and testing of an active mixing process will be valuable in determining if increased ester formation can be achieved. A simple paddle mixer may be employed and is expected to increase yields.

Of most importance is decreasing biodiesel production costs in a small-scale, on-farm system. Commodity prices contributed most to overall price per volume of biodiesel produced. However, this factor cannot be changed by the system operator. Likewise, chemical cost was another major expense, but the most economically favorable procedures were employed. Labor was the second largest expense. The largest portion of labor was required for mechanically extruding oil from the seeds. Future research should include means of automating the oilseed extrusion process in order to lower labor cost. Although the biodiesel processor was a fixed cost, it was substantial. Farmers typically have a great deal of mechanical aptitude and future research and efforts could focus on developing a biodiesel processor from materials a farmer may be able to easily and cheaply access. However this reactor would ideally contain timing relays to automate the reaction processes, safety measures to prevent pressure induced explosions, and an effective methanol recovery system.

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APPENDIX A

BIODIESEL PRODUCTION PROCEDURES AND CONVERSION EFFICIENCY REVIEW

A.1 Table of various transesterification techniques in published literature.

Oil Type	Catalyst (wt%)	Alcohol to oil (molar ratio)	Reaction time (hr)	Reaction Temp. (°C)	Ester yield (%)*†	Researcher‡
Soybean	NaOH (0.3)	EtOH (6:1)	1	30	NPS	1
				70		
		EtOH (12:1)	1	30	96.8	1
				70	97.2	
	NaOH (0.65)	EtOH (9:1)	1	50	95.8	1
	NaOH (1.0)	EtOH (6:1)	1	70	86.1	1
		EtOH (12:1)		30	91.3	1
		MeOH (3:1)	0.017	60	20.0	4
			0.033		28.0	
			0.067		33.0	
			0.5		60.0	
			1		62.0	
		MeOH (6:1)	0.1	32	64.0	4
			0.2		79.0	
			0.5		89.0	
			1		92.0	
			2		96.0	
			4		98.0	
			20		98.0	
			0.1	45	87.0	4
			0.2		91.0	
			0.5		93.0	
			1		97.0	
			0.017	60	86.0	4
			0.033		89.0	
			0.067		90.0	
			0.1		94.0	
			0.2		95.0	
			0.5		96.0	
			1		96.0	
	$NaOCH_3$ (0.5%)	MeOH (1:1)	1	60	41.0	4
		MeOH (2:1)			69.0	
		MeOH (3:1)			84.0	
		MeOH (4:1)			93	
		MeOH (5:1)			95.0	
		MeOH (6:1)	0.017	60	82.0	4
			0.033		88.0	
			0.067		90.0	
			0.5		97.0	
			1		98.0	
	KOH (1.0)	EtOH (6:1)	1	30	92.5	1

				70	93.3	
		EtOH (12:1)	1	30	95.1	1
				70	95.6	
		EtOH (30:1)	1	75	9.0	4
			2		20.0	
			5		58.0	
			20		90.0	
		MeOH (6:1)	48	60	72.7	2
	H_2SO_4 (1.0)	MeOH (30:1)	1	60	5.0	4
			2		5.0	
			5		8.0	
			20		50.0	
			30		55.0	
			45		82.0	
			50		90.0	
			69		92.0	
Soybean		n-BuOH (30:1)	0.1	114	10.0	4
			0.2		15	
			0.5		43.0	
			1		70.0	
			2		86.0	
			3		95.0	
			4		94.0	
		EtOH (6:1)	48	75	95.8	2
		MeOH (3.3:1)	48	60	76.5	2
		MeOH (3.9:1)			81.0	
	H_2SO_4 (3.0)	MeOH (6:1)	48	25	8.3	2
				45	57.2	
				60	88.7	
			96	60	95.1	2
		MeOH (20:1)	48	60	97.0	2
		MeOH (30:1)			98.4	
		n-BuOH (6:1)	48	110	92.1	2
		2-PrOH (6:1)	48	75	92.9	2
	H_2SO_4 (5.0)	MeOH (6:1)	48	60	95.0	2
		EtOH (3:1)	0.017	75	63.0	4
			0.033		68.0	
			0.067		70.0	
			0.5		76.0	
			1		80.0	
Sunflower	$NaOCH_3$ (0.5%)	EtOH (6:1)	0.017	75	75.0	4
			0.033		82.0	
			0.067		83.0	
			0.5		95.0	
			1		97.0	
		MeOH (1:1)	1	60	35.0	4
		MeOH (2:1)			68.0	

Sunflower	$NaOCH_3$ (0.5%)	MeOH (3:1)	0.017	60	60.0	4
			0.033		66.0	
			0.067		70.0	
			0.5		77.0	
			1		82.0	
		MeOH (4:1)	1	60	90.0	4
		MeOH (6:1)	0.017	60	78.0	4
			0.033		85.0	
			0.067		86.0	
			0.5		94.0	
			1		98.0	
		n-BuOH (3:1)	0.017	114	76.0	4
			0.033		75.0	
			0.067		76.0	
			0.5		77.0	
			1		88.0	
		n-BuOH (6:1)	0.017	114	90.0	4
			0.033		89.5	
			0.067		91.0	
			0.5		93.0	
			1		95.0	
Canola	KOH (1.4)	MeOH (4.6:1)	0.5	Room temp	91.9	3
	KOH (0.63) NaOH (0.90)	MeOH (3.0)	0.167	40	67.90 53.24	5
	$KOCH_3$ (2.38) $NaOCH_3$ (1.22)			50 60	94.27 89.13	
	$NaOCH_3$ (1.84) KOH (1.27) $KOCH_3$ (1.59) NaOH (0.45) $KOCH_3$ (0.79)	MeOH (4.5)	0.167	40 50 60	90.44 91.27 95.80 82.50 92.23	5
	$KOCH_3$ (1.59) $NaOCH_3$ (0.61) KOH (1.90) NaOH (1.35)	MeOH (6.0)	0.167	40 50 60	91.79 85.41 89.27 90.19	5 5
Cottonseed	$NaOCH_3$ (0.5%)	MeOH (2:1) MeOH (3:1) MeOH (4:1)	1	60	58.0 74.0 87.0	4
		MeOH (6:1)	0.017	60	53.0	4
			0.033		68.0	
			0.067		74.0	
			0.5		88.0	
			1		95.0	
Peanut	$NaOCH_3$ (0.5%)	MeOH (2:1) MeOH (3:1) MeOH (4:1)	1	60	62.0 78.0 87.0	4
		MeOH (6:1)	0.017	60	53.0	4

	0.033	68.0
	0.067	75
	0.5	91.0
	1	97.0

*NPS – No Phase Separation

†Not all ester yields presented are final yields. Some were measured during reaction.

‡Kucek et al. (2007)[1]; Canakci and Van Gerpen (1999)[2]; Dorado et al. (2004)[3]; Freedman et al. (1984a)[4]; Singh et al. (2006)[5]

APPENDIX B

EXPERIMENTAL EQUIPMENT AND CHEMICAL SPECIFICATIONS

B.1 Chemyx™ Nexus Model 6000 syringe pump

Weight	6 kg
Flow rate:	
Minimum:	1.56 pl/min (0.5 µl syringe)
Maximum:	200 ml/min (2000 ml syringe)
Step resolution:	0.046 µm
Accuracy:	± 0.35%
Reproducibility:	± 0.05%
Computer control:	RS232 COM port Windows XP, Vista, 7; Mac OS X v10 or later
Power requirements:	100-240 VAC: 50/60 Hz

B.2 Gast Manufacturing, Inc. vacuum pump model DOA-P704-AA

Power	115VAC / 4.2 A / 60 Hz / 0.1 kW
Size:	20 x 17 x 27 cm
Maximum pressure:	3103 mm Hg
Max vacuum:	84 kPag

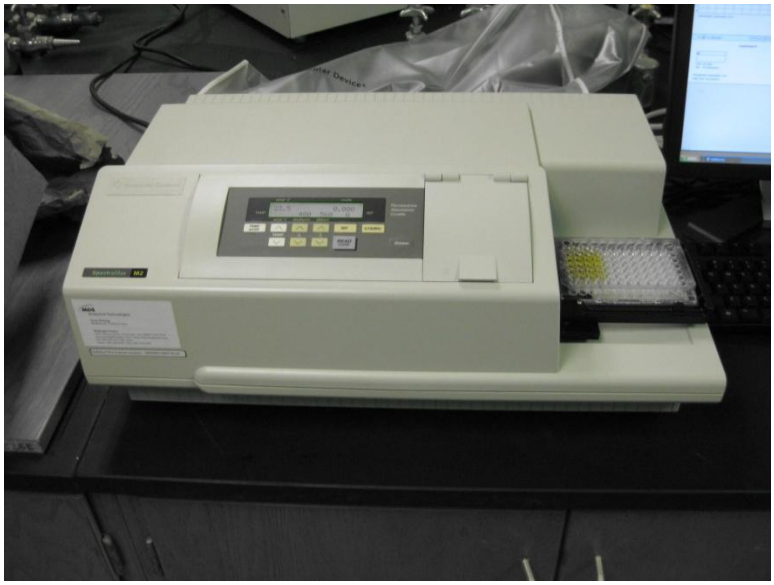
B.3 New Brunswick Scientific Innova 40 incubator shaker

Temperature:

Range:	5°C to 80°C
Control:	±0.1 °C
Uniformity:	±0.25 °C at 37 °C

Speed Range: 25 – 500 rpm (±1 ppm)

B.4 Molecular Devices Spectramax M2 Microplate Reader



Wavelength range:	200 - 1000 nm
Wavelength accuracy:	±2.0 nm
Wavelength selection:	Monochromator, tunable in 1.0-nm increments
Wavelength bandwidth:	≤ 4.0 nm
Wavelength repeatability:	±0.2 nm
Photometric resolution:	0.001 OD
Photometric accuracy (microplate):	< ±0.006 OD ±1.0%, 0–2 OD
Photometric range:	0–4.0 OD
Plate formats:	6, 12, 24, 48, 96, 384 wells
Light source:	Xenon flash lamp (1 joule/flash)
Detector:	Photomultiplier (R-3896)
Read time:	
96-well:	Abs 18 sec., FI 15 sec.
384-well:	Abs 49 sec., FI 45 sec.

B.5 Agilent Technologies Gas Chromatograph model 7890A

source: www.chem.agilent.com

Detector:	FID
Column:	10-m Restek biodiesel column with guard column

B.6 Henan Double Elephant Machinery Co., Ltd (Henan, China) model 6YL-120

Capacity:	6 T per 24 hours
Power:	15kW / 3ø / 1440 rpm
Size:	1970 x 700 x 780 mm
Weight:	680 kg

B.7 Karl Strähle GmbH & Co. KG (Dettingen, Germany) SK 60/2

Capacity:	720 kg/day
Power:	220 VAC / 1ø / 60 Hz
Size:	1300 x 2300 mm
Weight:	194 kg

B.8 Biodiesel Logic, Inc. BDL-55-SS-A

Capacity:	208 L per 8 hours
Filter:	14 micron
Vessel material:	304 SS
Power:	110/220 VAC / 1ø / 60 Hz / 30 A circuit
Heater assembly:	1ø / 316 SS
Pumps:	3 / 220 VAC / 0.4 kW
Weight:	907 kg
Dimensions:	183 cm x 66 cm x 213 cm

B.9 AMBERSEP™ BD 19

AMBERSEP™ BD19

Feedstock Purification Technology

AMBERSEP™ BD19 from Rohm and Haas

- Supplements or may replace conventional degumming processes
- Extends the life of the AMBERLYST™ BD20 esterification catalyst
- Improves operability of downstream manufacturing processes by removing troublesome foulants
- Removes foulants that contribute to the failure of ASTM and EN Biodiesel quality specifications

www.amberlyst.com

ROHM AND HAAS

Why AMBERSEP™ BD19?

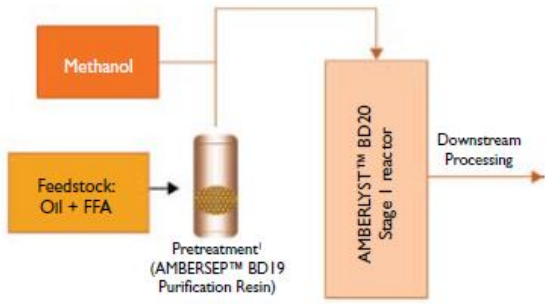
- Low Capital Investment for purification of your high free fatty acid feedstock
- High capacity for foulant removal per volume and cost of purification media
- High operability – responsive to variability in foulants and foulant levels
- Extends the lifetime of the AMBERLYST™ BD20 esterification catalyst. Mechanism for foulant removal is theoretically equivalent to catalyst aging mechanism

Ensuring consumers have confidence in the quality of the biodiesel they consume from your process is a top priority. With the shift away from pure vegetable feedstocks to higher free fatty acid oils and greases, maintaining this biodiesel quality can become more of a challenge. The AMBERSEP™ BD19 purification media removes unwanted species from the feedstock before they can affect the catalyst, process or final product quality.

Process Advantages

- Effective removal of both physical and chemical foulants
  - Cations, proteins, phospholipids
- Can reduce downstream equipment fouling
- Improved biodiesel and glycerine stream quality
- Helps prevent potential side reactions caused by unwanted components

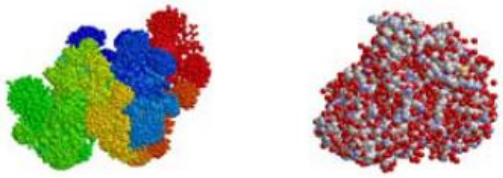
SIMPLE PROCESS AND EQUIPMENT FOR OIL PURIFICATION



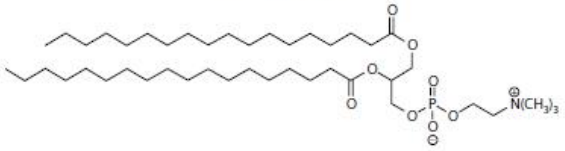
[1] Feedstock pretreatment may be recommended in order to meet local specifications and to extend catalyst lifetime

REMOVE PROBLEM FOULANTS FROM FEEDSTOCK

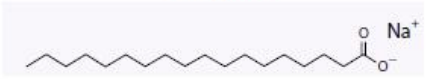
Proteins



Phospholipids



Ionic Species



B.10 AMBERLITE™ BD10DRY™ Biodiesel Purification Technology

Users Guide - Laboratory Trials

TO LAB TEST A SAMPLE OF AMBERLITE™ BD10DRY™ PURIFICATION MEDIA

To test Amberlite™ BD10DRY™ purification media we encourage you to use the "contaminated biodiesel" that has been well-separated from the glycerol phase after your transesterification process. This biodiesel should not be dried and preferably contains methanol traces. From experience, this phase usually contains less than 400 ppm of impurity cations from soap and catalyst. You can also prepare test solutions using pure biodiesel spiked with catalyst.

a) Column Purification Mode

Amberlite™ BD10DRY™ is a specialty polymer media that is most effective at removing impurities and glycerol traces when used in a "column mode". For lab testing, a glass column with roughly a 10:1 height:width ratio is recommended. A suitable column can be obtained from Ace Glass (Vineland, NJ; part number 5820-30; 25mm (1 inch) diameter by 300 mm (12 inch) length). A bed support must be used to keep the polymer beads in the column while allowing the biodiesel to easily flow through. Generally, glass frits or a stainless steel screen can be used for this purpose where the openings in the screen are no greater than about 0.18mm (80 mesh).

The column should be loaded about 1/4 full with biodiesel and the Amberlite™ BD10DRY™ media is then poured into the column. The presence of a liquid "heel" in the column helps to ensure uniform packing of the beads as they are loaded which minimizes possible channeling or flow distribution irregularities.
The column should be filled no more than 1/3 full with Amberlite™ BD10DRY™ media in order to allow for expansion of the resin as it removes impurities. Avoid contacting the media with pure methanol or water as this will cause it to swell up to 3 times in volume and the glass column can shatter if insufficient void space is left at the top of the column.

A liquid head of at least 25 mm (1 inch) should be maintained above the resin to prevent air infiltration into the bed. Gravity feed can then be used to pass contaminated biodiesel through the bed, although a pump will allow more precise control of flowrate.

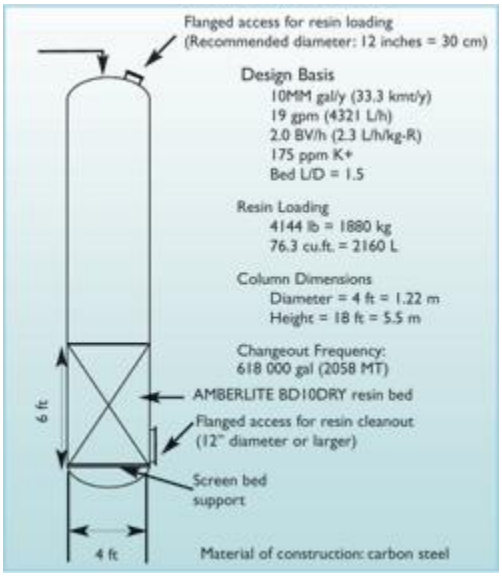
The flowrate of the biodiesel in the column should be around 3 L/hour of biodiesel per kg of Amberlite™ BD10DRY™ in the column (3.0 liters/hour per kg). With gravity flow, the flowrate can be easily controlled by using a pinchcock on a rubber hose connected to the column outlet fitting. The biodiesel recovered at the bottom of the column can then be analyzed.

b) Batch Purification Mode

Amberlite™ BD10DRY™ technology will yield the best results (lowest concentration of catalyst, soap, and glycerol in the treated biodiesel) when used in a column purification mode (see above). Use in a batch purification mode is therefore not recommended. It is, however, a quick and easy way to demonstrate the performance of Amberlite™ BD10DRY™ technology.

- Pour 10 g of Amberlite™ BD10DRY™ media into a glass vessel (e.g. a beaker).
- Add 100 mL of contaminated biodiesel and stir gently for one hour.
- Decant the biodiesel and analyze.

INDUSTRIAL USAGE



For a continuous process, it is recommended to install two columns to eliminate downtime when replacing spent resin. Please note that introducing a second column will not impact your consumption of Amberlite BD10DRY. The two columns are switched by valves to alternate between "lead" and "lag" treatment positions.

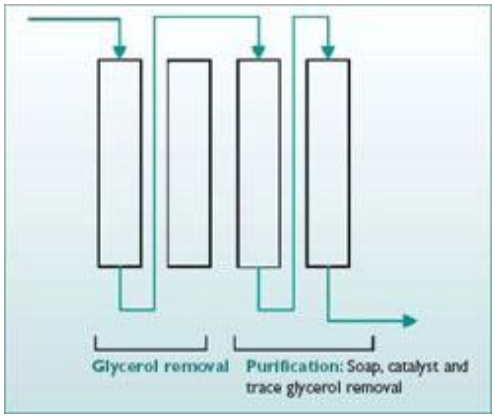
A Rohm and Haas Technical representative will work with you to select a column design best suited to your process.

A column design sketch based on 10 MM gallons (37.8 MM liters) per year throughput is enclosed.

CAUTION! Amberlite™ BD10DRY™ technology is designed to be used in a water-free process. The polymer beads will swell to up to 3 x their original volume as they absorb water. The beads will also swell over their life cycle as they remove impurities, including methanol and glycerol. It is therefore strongly recommended to leave sufficient void space in the columns.

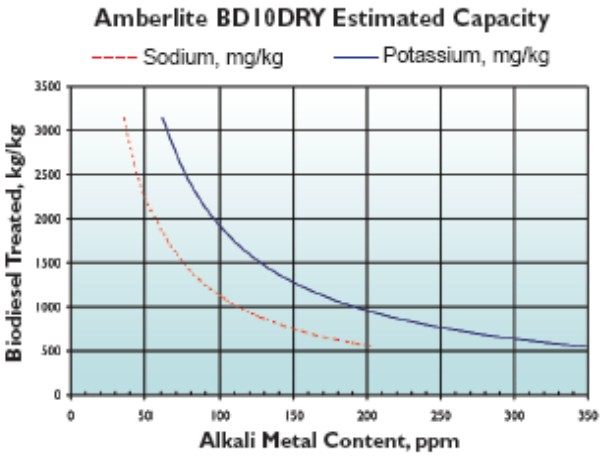
Extra glycerol removing capacity

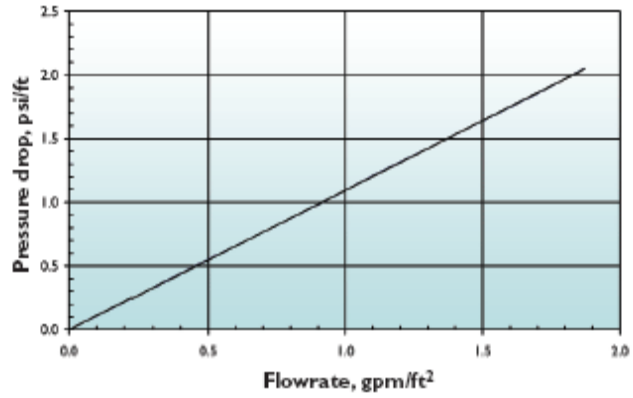
Even higher capacity for glycerol can be achieved by adding one or two extra columns of Amberlite™ BD10DRY™ media dedicated exclusively to glycerol removal, as shown in the following figure.

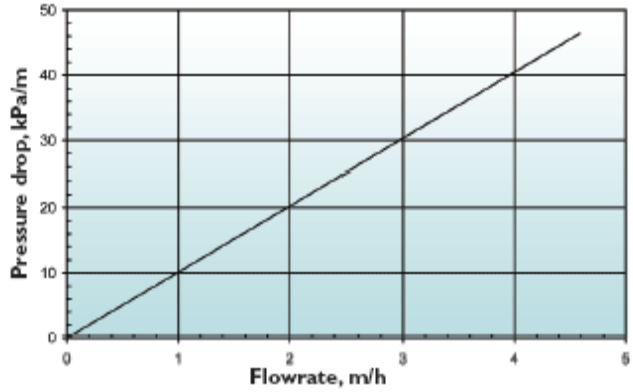


These additional glycerol removal columns are inserted just after the phase separation step. Note that the Amberlite™ BD10DRY™ media purchased for these columns will not impact your overall resin consumption. Why? Because when the glycerol removal columns are initially installed they will remove not only glycerol but also catalyst and soap. Therefore consumption of resin in the downstream purification columns will be saved.

When the media in a glycerol removal column is saturated with glycerol, the column can be egenerated by rinsing with methanol. The methanol solution coming off the column can then be sent back to the transesterification unit where the methanol is recycled. The interest in having two columns dedicated to glycerol removal is that the plant can continue to operate while the first column is being regenerated. These columns can thus be regenerated several times to reestablish their glycerol removing capacity. However their capacity to remove soap and catalyst is finite; in the steady state of operation they will only serve to remove glycerol. Under industrial conditions, the Amberlite™ BD10DRY™ media in the glycerol columns is usually replaced from time to time by the spent resin in the downstream purification columns.







B.11 Labconco© Purifier Biological Safety Cabinet

Source: www.labconco.com

- Nominal inflow velocity of 105 fpm (0.5 m/sec)
- Nominal downflow velocity of 55 fpm (0.3 m/sec)
- Interior-mounted, line-of-sight LCD information center with "Filter Life Remaining" bar graph, status line for alarm conditions and alerts to warn when filter life diminishes to 20%, 10% and 0%
- Filter monitoring system consisting of an electronically commutated motor (ECM) that delivers a precise volume of air as required and automatically adjusts as filters load without relying on airflow sensors
- Smart-Start™ System that allows the user to program start up and shut down operation
- Built-in interval or elapsed timer for experiment monitoring or UV light control (on models with UV light)
- Touchpad control on right-hand side post for manual activation of blower, light, timer, audible alarm mute and menu selection
- Radiused type 304 stainless steel interior and removable, seamless, dished work surface with lift out knobs
- Contain-Air™ Negative Pressure Channel
- Class 5 conditions per ISO 14644-1 and 2 (formerly Class 100)
- Supply and exhaust 99.99% efficient HEPA filters
- Two electrical duplex receptacles, (single outlets on 230 volt models), located one on each side, with ground fault interruption and stainless steel splash covers
- Fully-closing, clear 1/4" tempered safety glass sash with two sash handles; counterbalanced, anti-racking mechanism; and 10° slope
- 29" sash opening viewing height
- Bright, 100 foot-candle, glare-free fluorescent lighting located outside the contaminated work area
- Intrinsically safe negative pressure design
- 10" diameter exhaust outlet

APPENDIX C

OIL STORAGE EXPERIMENT REGRESSION TABLES.

C.1 WVO linear regression analysis for hydrolysis rate.

The GLM Procedure

Dependent Variable: FFA

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	3.31350000	3.31350000	190.03	<.0001
Error	7	0.12205556	0.01743651		
Corrected Total	8	3.43555556			

R-Square	Coeff Var	Root MSE	FFA Mean
0.964473	3.495372	0.132047	3.777778

Source	DF	Type I SS	Mean Square	F Value	Pr > F
time	1	3.31350000	3.31350000	190.03	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
time	1	3.31350000	3.31350000	190.03	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	2.602777778	0.09593019	27.13	<.0001
time	0.235000000	0.01704724	13.79	<.0001

C.2. Canola oil linear regression analysis for hydrolysis rate.

The GLM Procedure

Dependent Variable: FFA

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.98816667	0.98816667	113.91	<.0001
Error	7	0.06072222	0.00867460		
Corrected Total	8	1.04888889			

R-Square	Coeff Var	Root MSE	FFA Mean
0.942108	3.339593	0.093138	2.788889

Source	DF	Type I SS	Mean Square	F Value	Pr > F
time	1	0.98816667	0.98816667	113.91	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
time	1	0.98816667	0.98816667	113.91	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	2.147222222	0.06766286	31.73	<.0001
time	0.128333333	0.01202401	10.67	<.0001

C.3. Soybean oil linear regression analysis for hydrolysis rate.

The GLM Procedure

Dependent Variable: FFA

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	0.01350000	0.01350000	3.29	0.1126
Error	7	0.02872222	0.00410317		
Corrected Total	8	0.04222222			

R-Square	Coeff Var	Root MSE	FFA Mean
0.319737	25.06540	0.064056	0.255556

Source	DF	Type I SS	Mean Square	F Value	Pr > F
time	1	0.01350000	0.01350000	3.29	0.1126

Source	DF	Type III SS	Mean Square	F Value	Pr > F
time	1	0.01350000	0.01350000	3.29	0.1126

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	0.1805555556	0.04653562	3.88	0.0061
time	0.0150000000	0.00826960	1.81	0.1126

C.4 Test for hydrolysis slope homogeneity and interaction.

The GLM Procedure

Dependent Variable: FFA

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	63.72035185	12.74407037	1265.37	<.0001
Error	21	0.21150000	0.01007143		
Corrected Total	26	63.93185185			

R-Square	Coeff Var	Root MSE	FFA Mean
0.996692	4.413071	0.100357	2.274074

Source	DF	Type I SS	Mean Square	F Value	Pr > F
oil	2	59.40518519	29.70259259	2949.19	<.0001
time	1	2.86272222	2.86272222	284.24	<.0001
time*oil	2	1.45244444	0.72622222	72.11	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
oil	2	6.27945419	3.13972710	311.75	<.0001
time	1	2.86272222	2.86272222	284.24	<.0001
time*oil	2	1.45244444	0.72622222	72.11	<.0001

The GLM Procedure

Dependent Variable: FFA

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	63.72035185	12.74407037	1265.37	<.0001
Error	21	0.21150000	0.01007143		
Corrected Total	26	63.93185185			

R-Square	Coeff Var	Root MSE	FFA Mean
0.996692	4.413071	0.100357	2.274074

Source	DF	Type I SS	Mean Square	F Value	Pr > F
oil	2	59.40518519	29.70259259	2949.19	<.0001
time	1	2.86272222	2.86272222	284.24	<.0001
time*oil	2	1.45244444	0.72622222	72.11	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
oil	2	6.27945419	3.13972710	311.75	<.0001
time	1	2.86272222	2.86272222	284.24	<.0001
time*oil	2	1.45244444	0.72622222	72.11	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
compare soybean vs WVO	-0.10666667	0.01832251	-5.82	<.0001
compare soybean vs canola	-0.22000000	0.01832251	-12.01	<.0001
compare WVO vs canola	-0.11333333	0.01832251	-6.19	<.0001

APPENDIX D

IRRIGATION EXPERIMENT RESULTS BY CROP AND YEAR & IRRIGATION SCHEDULING SPREADSHEET EXAMPLE

D.1 2008 canola results.

Irr. TRT	Stand count		Dry yield		FFA		Oil		Protein		Biodiesel
(% Pan)	(plant/ha)	SD	(kg/ha)	SD	(%)	SD	(%DB)*	SD	(%DB)*	SD	Production (L/ha)
0	1,353,881	34,020	1,462	305	1.0	0.6	44.2	1.8	25.3	0.5	575.0
25	1,210,424	33,026	1,190	391	0.9	0.1	44.3	0.6	25.2	0.3	468.0
50	1,380,780	49,382	1,595	405	0.8	0.2	45.1	1.3	24.0	0.4	641.0
75	1,595,966	38,232	1,256	388	0.9	0.3	45.7	0.9	24.2	0.5	510.0
100	1,595,966	38,892	1,442	710	0.7	0.1	44.9	1.6	23.9	1.2	575.0
125	1,595,966	80,616	815	271	0.8	0.2	45.0	1.1	24.6	0.8	325.0

* (%DB) denotes dry basis percentage.

D.2 2010 canola results.

Irr. TRT	Stand count		Dry yield		FFA		Oil		Protein		Biodiesel
(% Pan)	(plant/ha)	SD	(kg/ha)	SD	(%)	SD	(%DB)*	SD	(%DB)*	SD	Production (L/ha)
0	1,226,563	40,677	2,507	159	0.5	0.1	42.9	1.0	22.67	1.18	957
25	1,200,740	220,626	2,801	223	0.4	0.1	43.2	1.5	22.52	1.13	1077
50	1,230,867	112,886	2,827	405	0.5	0.1	42.8	0.9	22.83	0.74	1077
75	1,196,437	225,552	2,623	268	0.6	0.2	43.6	1.3	23.07	0.93	1018
100	1,213,651	103,766	2,760	467	0.6	0.2	43.1	0.9	22.30	0.69	1059
125	1,325,549	310,187	2,521	685	0.5	0.1	43.2	0.5	22.69	0.81	969

* (%DB) denotes dry basis percentage.

D.3 2008 rotation 1 cotton results.

	Cotton Analysis				Cottonseed Analysis						
Irr. TRT	Stand count		Seed cotton yield		FFA		Oil		Protein		Biodiesel
(% pan)	(plants/ha)	SD.	(kg/ha)	SD	(%)	SD	(%DB)*	SD	(%DB)*	SD	Production (L/ha)
0	113,780	8,790	3,115	289	0.5	0.2	19.5	0.7	26.2	0.9	302
25	115,394	14,284	4,026	470	0.7	0.1	20.6	1.8	24.6	1.8	416
50	112,166	19,567	3,408	866	0.6	0.2	20.4	1.5	24.9	0.8	339
75	104,904	18,867	3,256	670	0.5	0.1	20.2	1.4	24.5	1.7	326
100	111,359	6,847	4,368	227	0.6	0.2	21.7	0.8	21.2	1.1	477
125	107,325	26,437	4,194	151	0.4	0.0	22.2	0.3	20.7	1.3	473

* (%DB) denotes dry basis percentage

D.4 2009 rotation 1 cotton results.

	Cotton Analysis				Cottonseed Analysis						
Irr. TRT	Stand count		Seed cotton yield		FFA		Oil		Protein		Biodiesel
(% pan)	(plants/ha)	SD	(kg/ha)	SD	(%)	SD	(%DB)*	SD	(%DB)*	SD	Production (L/ha)
0	111,669	26,134	3,015	111	8.1	2.5	22.6	1.1	22.4	1.5	344
25	101,072	31,045	2,802	157	6.7	2.4	22.1	0.6	22.7	1.7	321
50	108,408	27,327	2,949	226	10.0	3.5	22.0	0.7	23.3	2.2	327
75	107,593	37,836	2,632	573	7.8	1.5	22.3	1.8	21.0	1.1	301
100	119,820	18,894	3,037	107	11.5	2.5	23.2	0.4	20.9	0.6	358
125	97,812	22,900	2,711	190	10.3	1.3	22.2	1.0	21.1	1.2	306

* (%DB) denotes dry basis percentage

D.5 2009 rotation 2 cotton results.

	Cotton Analysis				Cottonseed Analysis						
Irr. TRT (% pan)	Stand count (plants/ha)	SD	Seed cotton yield (kg/ha)	SD	FFA (%)	SD	Oil (%DB)*	SD	Protein (%DB)*	SD	Biodiesel Production (L/ha)
0	101,888	20,339	3,188	302	14.3	2.6	21.6	1.3	24.4	0.2	333
25	104,333	13,311	2,962	185	10.5	1.7	21.4	1.1	23.3	1.5	314
50	96,997	16,915	3,042	225	8.6	2.9	21.4	0.7	23.4	2.2	328
75	107,593	8,418	3,458	335	12.1	1.7	21.8	1.0	23.3	2.3	291
100	96,182	22,352	3,005	908	7.5	1.8	22.6	0.7	20.5	2.8	363
125	92,921	24,615	3,150	549	9.1	5.3	22.5	0.3	22.2	2.0	304

* (%DB) denotes dry basis percentage

D.6 2010 rotation 1 cotton results.

	Cotton Analysis				Cottonseed Analysis						
Irr. TRT (% pan)	Stand count (plants/ha)	SD	Seed cotton yield (kg/ha)	SD	FFA (%)	SD	Oil (%DB)*	SD	Protein (%DB)*	SD	Biodiesel Production (L/ha)
0	122779	5,899	3,122	355	0.4	0.1	22.7	1.2	27.2	1.1	373
25	121,971	13,289	3,312	529	0.4	0.1	22.1	0.8	27.3	1.7	388
50	130,049	4,847	4,294	471	0.4	0.1	22.9	1.0	25.7	0.4	523
75	133,280	17,574	4,442	586	0.4	0.1	22.8	1.0	25.1	1.4	553
100	130,049	15,011	4,925	340	0.4	0.0	22.8	0.6	24.0	0.3	620
125	129,241	15,607	4,614	737	0.5	0.0	23.5	1.3	23.5	1.6	576

* (%DB) denotes dry basis percentage

D.7 2008 soybean results.

Irr. TRT (% Pan)	Stand count (plant/ha)	SD	Dry yield (kg/ha)	SD	FFA (%)	SD	Oil (%DB)*	SD	Protein (%DB)*	SD	Biodiesel Production (L/ha)
0	327,083	37,188	3,627	115	0.4	0.1	18.9	1.02	41.7	0.8	611
25	337,843	46,816	4,432	560	0.3	0.0	18.8	0.65	41.4	0.5	742
50	333,539	83,858	5,271	381	0.3	0.0	18.4	0.26	41.0	0.6	864
75	337,843	55,948	5,042	409	0.4	0.2	18.7	0.38	41.0	0.6	840
100	342,147	146,979	5,229	102	0.3	0.1	19.2	0.27	41.1	0.1	895
125	335,691	18,594	5,174	419	0.4	0.1	19.1	0.22	40.9	0.3	880

* (%DB) denotes dry basis percentage

D.8 2010 soybean results.

Irr. TRT (% Pan)	Stand count (plant/ha)	SD	Dry yield (kg/ha)	SD	FFA (%)	SD	Oil (%DB)*	SD	Protein (%DB)*	SD	Biodiesel Production (L/ha)
0	256,072	14,700	1,238	137	0.6	0.1	18.6	0.4	36.1	1.1	197
25	258,224	22,773	2,071	534	0.6	0.0	19.5	0.6	35.1	1.1	349
50	258,224	11,655	2,411	74	0.5	0.1	19.6	0.7	35.5	0.8	418
75	260,376	8,241	3,222	329	0.6	0.1	20.9	0.5	34.5	0.5	602
100	251,768	20,640	3,676	265	0.6	0.1	20.7	0.6	34.9	0.5	681
125	246,747	4,970	4,018	167	0.6	0.1	20.6	0.1	35.4	0.5	743

* (%DB) denotes dry basis percentage

D.9 Irrigation scheduling spreadsheet example. (continued on next two pages)

DATE	AWIS PAN (in)	CC (in.)	% CC	Rainfall (in.)	RUN-TIME (min) 25% CALC.	25% CUMUL.	25% TARGET	50% CALC.	50% CUMUL.	50% TARGET	75% CALC.	75% CUMUL.
7/1/2010	0.18	2	5%	0.00	0.15	0.68	0.00	0.30	1.37	0.00	0.46	2.05
7/2/2010	0.23	2	5%	0.00	0.19	0.88	0.00	0.39	1.75	0.00	0.58	2.63
7/3/2010	0.26	2	5%	0.00	0.22	1.10	0.00	0.44	2.19	0.00	0.66	3.29
7/4/2010	0.19	2	5%	0.00	0.16	1.26	0.00	0.32	2.51	0.00	0.48	3.77
7/5/2010	0.23	2	5%	0.00	0.19	1.45	0.00	0.39	2.90	0.00	0.58	4.35
7/6/2010	0.26	2	5%	0.00	0.22	1.67	0.00	0.44	3.34	0.00	0.66	5.01
7/7/2010	0.26	4	10%	0.00	0.44	2.11	0.00	0.88	4.21	0.00	1.31	6.32
7/15/2010	0.24	8	20%	0.00	0.81	5.92	0.00	1.62	11.85	0.00	2.43	17.77
7/16/2010	0.29	8	20%	0.00	0.98	6.90	0.00	1.96	13.80	0.00	2.93	20.71
7/17/2010	0.20	8	20%	0.11	0.67	7.58	0.00	1.35	15.15	0.00	2.02	1.73
7/18/2010	0.12	8	20%	0.00	0.40	7.98	0.00	0.81	15.96	0.00	1.21	2.94
7/19/2010	0.19	10	25%	0.01	0.80	8.78	0.00	1.60	17.56	0.00	2.40	5.34
7/20/2010	0.16	10	25%	0.00	0.67	9.46	0.00	1.35	18.91	0.00	2.02	7.37
7/21/2010	0.24	10	25%	0.00	1.01	10.47	0.00	2.02	20.93	21.00	3.03	10.40
7/22/2010	0.30	20	50%	0.00	2.53	12.99	0.00	5.06	4.99	0.00	7.58	17.98
7/23/2010	0.30	20	50%	0.00	2.53	15.52	0.00	5.06	10.04	0.00	7.58	25.57
7/24/2010	0.33	20	50%	0.00	2.78	18.30	0.00	5.56	15.61	0.00	8.34	7.91
7/25/2010	0.37	20	50%	0.00	3.12	21.42	21.00	6.24	21.84	22.00	9.35	17.26
7/26/2010	0.30	26	65%	0.00	3.29	3.71	0.00	6.57	6.42	0.00	9.86	27.12
7/27/2010	0.25	26	65%	0.00	2.74	6.45	0.00	5.48	11.89	0.00	8.22	8.34
7/28/2010	0.22	26	65%	0.00	2.41	8.86	0.00	4.82	16.71	0.00	7.23	15.57
7/29/2010	0.22	26	65%	0.00	2.41	11.27	0.00	4.82	21.53	22.00	7.23	22.80
7/30/2010	0.16	30	75%	0.52	2.02	13.29	0.00	4.04	3.58	0.00	6.07	5.87
7/31/2010	0.25	30	75%	0.00	3.16	16.45	0.00	6.32	9.90	0.00	9.48	15.35
TOTAL	**7.27**			**1.81**			**21.00**			**65.00**		

RUN-TIME (min)							ACTUAL IRRIGATION APPLIED (in)				
75% TARGET	100% CALC.	100% CUMUL.	100% TARGET	125% CALC.	125% CUMUL.	125% TARGET	25%	50%	75%	100%	125%
0.00	0.61	2.73	0.00	0.76	3.41	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.78	3.51	0.00	0.97	4.38	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.88	4.38	0.00	1.10	5.48	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.64	5.02	0.00	0.80	6.28	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.78	5.80	0.00	0.97	7.25	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.88	6.67	0.00	1.10	8.34	0.00	0.00	0.00	0.00	0.00	0.00
0.00	1.75	8.43	0.00	2.19	10.53	0.00	0.00	0.00	0.00	0.00	0.00
0.00	3.24	3.70	0.00	4.04	7.62	0.00	0.00	0.00	0.00	0.00	0.00
21.00	3.91	7.61	0.00	4.89	12.51	0.00	0.00	0.00	0.30	0.00	0.00
0.00	2.70	10.30	0.00	3.37	15.88	0.00	0.00	0.00	0.00	0.00	0.00
0.00	1.62	11.92	0.00	2.02	17.90	0.00	0.00	0.00	0.00	0.00	0.00
0.00	3.20	15.12	0.00	4.00	21.90	22.00	0.00	0.00	0.00	0.00	0.31
0.00	2.70	17.82	0.00	3.37	3.28	0.00	0.00	0.00	0.00	0.00	0.00
0.00	4.04	21.87	22.00	5.06	8.33	0.00	0.00	0.30	0.00	0.31	0.00
0.00	10.11	9.98	0.00	12.64	20.97	21.00	0.00	0.00	0.00	0.00	0.30
26.00	10.11	20.09	20.00	12.64	12.61	0.00	0.00	0.00	0.37	0.29	0.00
0.00	11.12	11.21	0.00	13.90	26.52	27.00	0.00	0.00	0.00	0.00	0.39
0.00	12.47	23.69	24.00	15.59	15.11	0.00	0.30	0.31	0.00	0.34	0.00
27.00	13.15	12.83	0.00	16.43	31.54	32.00	0.00	0.00	0.39	0.00	0.46
0.00	10.96	23.79	24.00	13.69	13.23	0.00	0.00	0.00	0.00	0.34	0.00
0.00	9.64	9.43	0.00	12.05	25.28	25.00	0.00	0.00	0.00	0.00	0.36
23.00	9.64	19.07	0.00	12.05	12.33	0.00	0.00	0.31	0.33	0.00	0.00
0.00	8.09	27.16	27.00	10.11	22.45	22.00	0.00	0.00	0.00	0.39	0.31
0.00	12.64	12.80	0.00	15.80	16.25	0.00	0.00	0.00	0.00	0.00	0.00
97.00			**137.00**			**171.00**	**0.30**	**0.93**	**1.39**	**1.96**	**2.44**

2010 Montly Totals				---------- Irrigation Applied (in.) ----------				
Sprinkler West	Days	AWIS PAN (in.)	Rainfall (in.)	25%	50%	75%	100%	125%
March	31	2.64	4.13	0.00	0.00	0.00	0.00	0.00
April	30	5.42	2.52	0.00	0.00	0.00	0.00	0.00
May	31	4.83	5.41	0.00	0.00	0.00	0.00	0.00
June	30	5.66	2.24	0.00	0.00	0.00	0.00	0.00
July	31	7.27	1.81	0.30	0.93	1.39	1.96	2.44
August	31	7.57	1.22	1.94	3.54	5.33	7.27	9.03
September	30	7.12	1.08	1.64	3.60	5.19	6.94	8.71
October	31	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Season Total	**245**	**40.5**	**18.4**	**3.9**	**8.1**	**11.9**	**16.2**	**20.2**
Jun-Jul-Aug	**92**	**20.50**	**5.27**	**2.24**	**4.47**	**6.71**	**9.23**	**11.47**
Nov - Apr			**26.71**					
Canola (bu/ac, MMC)			**44.8**	**50.0**	**50.5**	**46.8**	**49.3**	**45.0**
Total water (in/ac, Nov - Apr)			**26.7**	**26.7**	**26.7**	**26.7**	**26.7**	**26.7**
Water prod, bu/in			**1.7**	**1.9**	**1.9**	**1.8**	**1.8**	**1.7**
Soybean (bu/ac, MMC)			**18.4**	**30.8**	**35.9**	**47.9**	**54.7**	**59.8**
Total water (in/ac, May-Sept)			**11.8**	**15.6**	**19.8**	**23.7**	**27.9**	**31.9**
Water prod (bu/in)			**1.6**	**2.0**	**1.8**	**2.0**	**2.0**	**1.9**