AN ENERGY ANALYSIS AND CHARACTERIZATION OF SAFOU (*DACRYODES EDULIS) AS BIOFUEL FEEDSTOCK.*

A Thesis
by
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ABSTRACT

AN ENERGY ANALYSIS AND CHARACTERIZATION OF SAFOU
(*DACRYODES EDULIS*) AS BIOFUEL FEEDSTOCK
(December 2010)

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Safou (*Dacryodes edulis*) is a fruit indigenous to West Africa with considerable potential as an oil crop. The current market for Safou fruit experiences as much as 40-50% post-harvest losses en route to market. The need for a strategy to recover value lost due to fruit spoilage and Safou's potential as a biodiesel feedstock have been combined in this work. In ideal terms, oil extracted from the spoiled crop could offset fuel production costs or even produce the fuel to transport the crop to market, thereby increasing food security in areas of West and Central Africa where Safou is prolific. In this work, the embodied energy of Safou pulp, seed, press-cake, and the oil generated from pressing pulp was quantified. Energy required for processing was also quantified, and preparing and pressing spoiled pulp were investigated in terms of both oil yield and character of the oil. Both fresh and spoiled pulp oil were investigated in terms of fuel characteristics and found to be similar. Fuel was

produced from the pulp oil and compared to conventional petro-diesel and soy biodiesel in terms of emissions when combusted in a 2006 Jetta TDI.

According to the findings of this research, Safou has potential as a biofuel feedstock. Although the energy balance assessment conducted did not represent a comprehensive life cycle analysis, the potential energy balance of Safou as biodiesel feedstock was found to be favorable. The prospect of reclaiming post-harvest losses by extracting oil from spoiled fruit pulp was found to be possible. Emissions generated by Safou were not uniquely better or worse than those of petro diesel or biodiesel, despite some variation in emissions performance under different conditions. Although the Safou industry is in its infancy, the potential to develop it further without compromising its continued use as a food source appears feasible, since spoiled fruit was shown to be a feasible source of oil for biodiesel production.

DEDICATION

To my father, who showed me how to dream and taught me how to build, and my mother, who always nurtured my creativity.

To my wife, who made this possible with her loving support and patience.

To my children, who with their innocent and elegant creativity remind me of what is precious in life.

ACKNOWLEDGMENTS

My three year old daughter has asked me many times over the last couple of months "are you still working your 'phesis'?" I look forward to saying no. This process has been the most educational experience that I have ever pursued in terms of academic and personal challenges. It has also been the most humbling. As the final draft is near completion, I am increasingly aware of how in debt I am to the many people that have helped me. While it may be my thesis, saying so almost feels a little crass because I have depended on so many people to get this done.

First and foremost I'd like to thank Molly not only for being my best friend, but an amazing wife and mother. From finding the program at Appalachian State University to editing parts of this thesis you have been a major part of all of this. You have encouraged and supported me in countless ways. You have shared in countless frustrations and I look forward to sharing in the success of finishing this work. From the bottom of my heart thank you. I'd also like to thank my children Sophia and Xander. You probably won't remember much of the past two years but I certainly will. You guys have been a much needed distraction when my "phesis" has been overwhelming and you have been a foundational motivation to finish. I only hope it all helps me to be a better father. Papa loves you very much.

Secondly, I would like to thank the members of my thesis committee first as a group and then individually. Dr. Hoepfl, Dr. Raichle and Dr. Ramsdell, it has been almost three years since I came to visit the Technology Department for the first time. I recall very well speaking to all three of you and while it was obvious that you were very busy you were also very welcoming. From the beginning I admired you but I had no idea just how dedicated the

three of you were to education and the practical application of what is learned. You are wise lot and it has been a blessing to be your student.

Dr. Hoepfl, thank you for being the chair of my thesis committee and working so hard through draft after draft. You are a skilled wordsmith and have an inspiring, and in this case much needed, organizational gift. I am profoundly in debt to you not only for all your help but also for your encouragement. You care deeply about education but even more so about those whom you teach. I'm not the only one you have inspired or cared for but I feel extremely blessed to have been one. Thank you.

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Dr. Ramsdell, thank you for your leadership and graciousness. Being on the biofuels team that eventually led to the work done for this thesis has been a genuine pleasure. Thank you for allowing me to work with you not only on this thesis but on the biofuels emissions project as well. Your ability to see the advantage in disadvantage or potential behind an apparent dead end is a rare and redemptive gift. Thank you.

Jeremy Ferrell, thank you for inspiring me to pursue biofuels. While I had leanings towards it before coming into the program your commitment to the field and your desire to take academic learning and apply it practically has been an example which I wish to imitate. Thank you.

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I'd also like to thank Dr. Joseph Kengue for pioneering safou research. Primarily I must thank him for the considerable effort and work that has laid the foundation for safou to better people's lives. Secondly, I'd like to thank him for being gracious enough to send me valuable literature on the subject. Ce travail aurait été impossible avec la fondation que vous déposer devant ceux d'entre nous vient derrière. Je pary que vous le trouvez acceptable et peut-être utile.

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The success of my time in the DRC was made possible by several people. First, I'd like to thank my parents who provided a place for me to stay and a location to do all the work necessary to export the safou samples. Secondly, I'd like to thank Papa Akula Paul Mukanga, a life-long friend who was an invaluable companion during the whole process of acquiring and preparing fruit pulp for export to the United States. Thirdly, I'd like to thank, Papa Jean, Omba Ngandu, and Mbutshu Ngandu, for their help processing the fruit pulp. Fourthly, I'd like to thank Wendy Bernhart for making the collection of safou in Kimpese possible. Fifthly, I'd like to thank the Trapps, the Gorenflos, and the Sthreshleys for providing dehydrators and allowing me to use their ovens for drying "that stinky fruit". Lastly, I'd like to thank Rusty and Debbie Pugh as well as my aunt Marty Law for being willing to carry samples of the dried fruit pulp to the US in their luggage.

Finally I'd like to thank the people that helped by taking care of Sophia and Xander while I had to work. Thank you to the Barbees, particularly Laura and her daughter Ann for making leaving your house so hard for my kids. Thank you to the Berry's for treating us like an extension of your family I know Sophia felt like your fifth daughter. Thank you to the Revels. It doesn't bother me one bit if my kids want to be like yours. And finally thank you to Gran-Mary who clearly loves her grandkids.

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CHAPTER 1

INTRODUCTION

The global trend toward increased use of renewable energies has led to the investigation of non-traditional oil producing crops. Some crops have been discovered in the tropical sub-Saharan regions of Africa that have potential for use as biofuel feedstocks. One promising example is the fruit of the *Dacryodes edulis* tree. This tree is found in Western Africa and its fruit, commonly known as Safou, has primarily been cultivated as a food source, but the tree is also a source of shade, wood, and traditional medicines (National Research Council, 2008).

Safou was selected for research and domestication by the World Agroforestry Center (ICRAF) in the early 1990s (Franzel, Jaenicke, & Janssen, 1996; Jaenicke, Franzel, & Boland, 1995). Since that time research has been initiated to characterize the fruit's chemical, nutritional, and market potential as well as the tree's agroforestry potential. An expanding Safou market has encouraged these efforts (Awono, Ndoye, Schreckenber, Tabuna, & Isseri, 2002), and the fruit's oil content, in particular, has drawn significant attention. The fruit crop from *Dacryodes edulis* is estimated to yield more oil than commercialized oil crops like coconut and oil palm (El Bassam, 1998).

Many of the obstacles for growing and marketing Safou have been identified, but not all have been satisfactorily addressed. The variability of trees and their fruit has confounded farmers and consumers alike. Furthermore, food crop losses en route to markets have been estimated as high as 50% due to harvest, post-harvest handling, and the fruit's inherently short shelf life in tropical climates (Silou, Massamb, Maniongui, Maloumbi, & Biyoko, 2006). Although the fruit has not been easy to commercialize, the market demand continues to grow. Safou's lipid content and possible annual production rate have garnered serious consideration by members of the food, cosmetics, and fuel industries (Arisa & Aworh, 2008). The fruit's food potential has been extensively investigated and the oil's lipid characteristics have identified it as a potential raw material for cosmetics. Regarding its use as a fuel, however, little has been done to seriously analyze the energy content of the fruit or to characterize the oil's potential if converted into biodiesel.

Statement of the Problem

Though primarily a food crop, Safou's potential to be one of the highest oil-producing fruit crops begs the question of its potential as a biofuel crop. Because Safou has a large post-harvest loss rate (40-50%), there is potential to recuperate that loss by processing an otherwise spoiled food product into two marketable products, oil and press cake. Though these products may not be favorable for human consumption oil may still be used for cosmetics and fuel while the meal could be used for animal feed. In ideal terms, fuel generated by the otherwise lost crop could offset or even produce the fuel to transport the crop to market, thereby increasing food security in areas of West and Central Africa where Safou is prolific. While there is potential for recuperating post harvest losses through oil extraction and fuel production, such a path is contingent on basic issues of biofuel viability regarding energy balance and fuel characteristics.

Purpose of the Research

The purpose of this research is to investigate the viability of Safou as a biodiesel feedstock in terms of its energy content and fuel characteristics. A favorable energy balance, where the energy contained in a fuel is greater or at least equal to the energy needed for production, is key to viability. The fuel's pre-combustion and combustion characteristics such as cloud point, gel/pour point, lubricity, viscosity, and flashpoint help to define the fuel and its regional viability while the post-combustion emissions place the fuel in context of green house gas (GHG) emissions compared to other fuels.

The Scope of the Research

The scope of this work involved six main tasks. The first task was to quantify the energy densities of the raw oil and of the residual biomass generated during oil production; this included the press meal and seeds. The second task was to produce a Safou biodiesel that could pass general ASTM certification. The third task was to quantify the energy density of the oil once converted to Fatty Acid Methyl Ester (FAME) biodiesel. The fourth task was to generate a preliminary physical and chemical characterization of the Safou biodiesel and to confirm general adherence to ASTM certification prior to combustion. The fifth task was to generate three distinct emissions data sets from the combustion of Safou bio-diesel, standard petro-diesel, and soy biodiesel. The sixth task was to then compare the post-combustion emissions generated from each fuel in terms of CO, CO_2, NO, NO_2, and total hydro-carbons (THC).

Limitations of the Study

Safou Fruit Sample

Fruit origin and morphology. There is a large variety of Safou fruits in western Africa. Unlike other fruits, such as apples, where there are specific cultivars with names and consistent fruit morphology, the nomenclature for Safou varieties is not well developed. In the absence of cultivar identification for this research the fruit has been identified by geographical origin and fruit morphology. The samples collected for this study were from the area around the town of Kimpese in the Bas-Congo region of the Democratic Republic of Congo (DRC). The fruit available there can generally be categorized into three groups based on size. The largest were on average 8 cm long and 3.5 cm in diameter, the medium-size fruits were 5.5 cm by 3.2 cm in diameter, and the smallest fruits were 3.75 cm long and 3 cm in diameter.

Sample validity. Ideally, a significant sample size of a single fruit type within a uniform stage of ripeness would have been available for the study; however, fruit availability was limited. The three fruit sizes and the stages of ripeness were indicative of what kind of Safou is grown in the area and is typically harvested for market. That said, it cannot be assumed that the fruit collected in this sample was representative of all Safou fruit that goes to market.

Fruit ripeness. Due to a delayed fruiting season attributed to diminished rains during the months preceding January 2010, when this sample was collected, a sufficient quantity of uniformly and ideally ripe fruit was not available. The only criterion for inclusion in the sample was edibility based on ripeness. Included fruit was near-ripe and ripe, but no over-ripe fruit was available. It has been suggested that the longer a fruit is left on the tree the greater the oil content. It was not possible to confirm this claim or to quantify the oil production potential for fruit that has spoiled on the tree.

Fruit oil yield. The amount of oil contained in the Safou fruit is dependent on the variety, the growing conditions, and the fruit's stage of maturation. As a rule there is a greater percentage of oil in the pulp the longer the fruit remains attached to the tree. Due to the lack of overripe fruit for this sample, estimates of the fruit's potential maximum oil yield were not directly attainable. However, in light of what kind of fruit is moved to market the sample collected is a reasonable representation, because more than 60% were directly purchased from producers moving fruit to market or from local markets. The remaining fruit was harvested expressly for this study. Of these fruit, more than half were ripe and the rest near-ripe. This means that about 80% of the fruit was market ripe.

Fruit Harvesting Data

Data collected for harvesting represented a very small sample and were limited to six trees of varying sizes. A Safou tree can grow to be more than 25 meters tall, making it difficult and dangerous to collect fruit. Two of the trees from which fruit was collected were very accessible, while the other four were less so. The harvesting data, though not extensive or general, can provide some foundation as to the time required for harvesting by hand and to potential tree crop development.

Process and Preparation of Oil and Fruit Pulp for Export

Oil processing. A quantity of oil was extracted in the DRC by drying the fruit and pressing out the oil using a manual press. This raw oil was placed in canning jars with loose lids, which were then placed in a bath of boiling water for 10 minutes. The lids on the jars where then tightened and allowed to cool and seal.

Fruit pulp processing. Three methods were employed to prepare fruit pulp for export. The first method included removing the firm pulp from the seed center, chopping the pulp, and drying it in electric forced-air dehumidifiers. The dehumidifiers operated between 135° F and 155° F for 7-9 hours. The second method also included removing and chopping the pulp, but these samples were spread on baking trays and placed in electric ovens at ~250° F until they sounded brittle and were no longer soft when pinched. The third method included placing fresh and rotting pulp in canning jars and pressure canning at 15 psi, which is equivalent to 250° F. The varying methods of preparation have differing effects on the pulp at a cellular level, but are expected to have less effect on the character of the oil. It is not a primary goal of this research to compare these three treatment methods. Furthermore, these methods of pre-treatment for oil extraction are not indicative of a preexisting process used in western Africa because oil extraction is not a common practice for this fruit. Ideally, the most common and energy efficient method would have been, used but this has not been determined as of yet.

Energy Analysis and Considerations

Energy is a focus of this research only in terms of the energy embodied in the oil, the press-cake, the seeds, and the biodiesel. Energy life cycle for the process and production of fuel is not a primary focus of this research. That said, some preliminary data for energy inputs was collected and was considered for harvesting, preparing, drying, and pressing the fruit, but these data are preliminary and only provide some context for future consideration of energy inputs in relation to the embodied energy of the fuel.

Fuel Characterization

The pre-combustion characterization for the oil and fuel did not include the complete battery of tests required for American Society of Testing and Materials (ASTM) certification. However, partial ASTM characterization was possible at Appalachian State University (ASU) using gas chromatography/ mass spectrometry (GC/MC) and hydrogen nuclear mass resonance (HNMR). Also, lubricity was tested following ASTM protocol with a high frequency reciprocating rig (HFRR). Physical fuel characteristics, including cloud point and gel point, were investigated using practical bench top tests but did not strictly follow ASTM protocol. Further ASTM tests were performed at Pittsboro Community College by Jeremy Ferrell, a Research Analyst for Appalachian State University's Energy Center. These tests followed ASTM certified testing protocol and are summarized in Table 4.7.

Fuel Sample

The fuel sample used for the emissions data only included two gallons of polished fuel. Although this was not a substantial quantity it was sufficient to identify obvious fuel characteristics and emissions.

Engine Type

The emissions data generated for this study were collected from the operation of a 2006 VW Jetta TDI. This vehicle is not representative of all diesel engines or vehicle types.

The Jetta engine has four in-line cylinders with a total volume of 1,896 cc. The cylinders have a 79.5 mm bore diameter and a stroke length of 95.5 mm. This generates a compression ratio of 18.5:1. The engine has two overhead cams per cylinder. The fuel delivery system is a direct injection system. The engine also has a turbo compressor. Assuming the use of petro-diesel, the engine is estimated to generate 75kW (100 HP SAE) running at 4,000 rpm. It can generate 240 Nm (177 lb/ft) of torque at 1800 rpm.

Catalytic Converter

The 2006 VW Jetta TDI is equipped with a three-way catalytic converter designed toconvert NO_2 to N_2 and O_2 while converting CO and hydrocarbons to CO_2 and water.

The Driving Course

Unlike many vehicle emissions tests where vehicles are placed on a stationary dynamometer, the emissions data for this study were collected on-road under real driving conditions. A five-mile section of US Highway 421 east of Boone, North Carolina was selected because it presented variation in the terrain and distance that would accommodate several runs with the fuel supply available. This section of road is not indicative of all driving conditions but simply provided a basis of comparison between Safou biodiesel and other fuels. A more detailed description of the course is presented in Chapter 4 along with emissions data.

Research Questions

RQ1: How much energy is embodied in Safou pulp, raw Safou oil, residual press-cake, and Fatty Acid Methyl Esters (FAME) biodiesel generated from the oil?

RQ2: What are the characteristics of Safou oil extracted from fruit pulp that has spoiled and has become inedible?

RQ3: What are the fuel characteristics (including GS/MS, HNMR, lubricity, flash point, cloud-point, and gel-point) of biodiesel (FAME) made from Safou oil?

RQ4: What kind of emissions profile does Safou FAME fuel generate when combusted in a 2006 Volkswagen Jetta TDI engine, and how does the profile compare to petro-diesel and soy biodiesel fuel run under similar conditions?

Definition of Terms

GC/MS –Gas Chromatography-Mass Spectrometry. This uses gas-liquid chromatography and mass spectrometry to identify differing substances at the molecular level within a test sample.

H-NMR – Hydrogen-Nuclear Magnetic Resonance. This is used to investigate molecular structure by exposing hydrogen atoms to magnetic fields and electromagnetic impulses. How the molecule resonates indicates location of hydrogen and consequently molecular structure.

Gel point/Pour point – The temperature at which a fuel ceases to flow and congeals.

Cloud Point– The temperature at which a fuel ceases to be clear and molecules begin to clump together.

FAME– Fatty Acid Methyl Ester: Biodiesel made with methanol.

FAEE– Fatty Acid Ethyl Ester: Biodiesel made with ethanol.

TDI– Turbo Direct Injection: This refers to a diesel engine that has a turbo charger compressing air that is going into the combustion chamber, but also indicates how the fuel is being delivered into the combustion chamber.

CO – Carbon Monoxide: In reference to combustion, presence of this gas is indicative of an incomplete combustion.

CO_2– Carbon Dioxide: This gas is indicative of a complete combustion where a single carbon has been completely oxidized and is molecularly stable.

NO– Nitric Oxide: Can be indicative of nitrogen in the fuel but more commonly is a byproduct of combustion heat and resulting oxidization of atmospheric nitrogen in the cylinder.

NO_2 -Nitrogen Dioxide: A byproduct of in-cylinder combustion following NO formation, but also is produced in the exhaust stream by further oxidization of NO.

THC—Total Hydrocarbons: Total non-methane hydrocarbons indicative of incomplete combustion in cylinder.

Significance of the Study

Characterizing the potential of Safou oil for fuel purposes has several implications. Communities in West African countries are significantly dependent on financial gain from agrarian enterprise. A crop that experiences a post-harvest loss in excess of 40% in areas where malnutrition is prevalent is a problem for social health as well as for the economies of operation. The potential to reclaim that lost percentage for either food or other purposes is advantageous for producers and consumers alike.

Furthermore, the development of crops with indigenous appeal can strengthen the agricultural and energy sectors of struggling economies. Identifying the oil's fuel qualities, whether favorable or not, will help to inform future crop and industry development. Defining the fruit's biofuel potential will also inform international investment and research into developing the crop for food, fuel, or a combination of the two while keeping in mind food and fuel security.

The potential of another oil crop that requires less land than traditional crops such as soy or palm would be favorable in terms of land use. The fruit's general appeal as a food has established a market that is growing. The crop's intrinsic characteristics recommended it for agroforestry systems. Furthermore, crop production is at present decentralized and any industrial development that used the fruit's oil either for food, cosmetics, or fuel could have a positive decentralized economic impact. A decentralized agro-fuel industry is key to the sustainability of the industry itself but also would support the transport of produce to markets.

CHAPTER 2

REVIEW OF LITERATURE

Safou as an Energy Crop

Though mentioned as a possible feedstock for biodiesel, no research has been done to identify Safou oil's fuel characteristics as a straight vegetable oil (SVO), a fatty acid ethyl ester (FAEE), or a fatty acid methyl ester (FAME). There are obstacles to its development as a biodiesel feedstock and investigations into the embodied energy and processing burden for oil removal have been limited. Quantifying the energy density of the fruit pulp, seeds, oil, and press meal are essential steps in investigating energy potential. A preliminary understanding of the energy demand to extract oil is essential to defining the obstacles and potential paths to processing. Testing the Safou biodiesel fuel emission profile will provide information that quantifies whether a liquid fuel is desirable in terms of energy delivered and of greenhouse gas (GHG) production. Not every oil feedstock is suitable for oil harvesting operations due to an unfavorable energy balance or poor quality of the end product. It is also important to consider the larger socio-economic implications of such a development and place them in context of the food vs. fuel debate.

The impetus for this research was founded on the fact that Safou crop losses en route to markets have been estimated as high as 50% (Silou et al., 2006) Methods of mitigating post-harvest loss have been investigated with some success. However, developing a process, product, and market for the lost material may be a better use of available resources in a tropical setting. The fruit's current oil production potential and its genetic variability that may promise even more oil demands further consideration by food, cosmetics, and fuel industries (Arisa & Aworh, 2008).

Biodiesel in a Global Context

Growth Trajectory

Energy is vital for socio-economic development (Demirbas, 2009). Social and economic dynamics are global, as are the problems associated with securing energy and food supplies. Vegetable oil crops, both edible and non-edible, are being investigated and grown in larger quantities throughout the world in developed and developing countries alike (Pahl, 2008). World population is expected to grow, placing greater demands on a finite fossil energy supply. According to the US Energy Information Administration's *2010 Energy Outlook*, marketed energy consumption is projected to grow from 495 quadrillion Btu in 2007 to 739 quadrillion Btu by 2035. This represents a 49% increase in global energy demand (U.S. Department of Energy [DOE], 2010). Liquid fuels in 2007 accounted for 35% (174 quadrillion Btu or 86.1 million barrels) of daily global energy consumption. The IEO2010 reference case predicts that by 2035 liquid fuels will make up only 30% of daily global energy consumption but will have increased to 223 quadrillion Btu or 110.6 million barrels a day. Biofuels are projected to increase from 1.17 million barrels per day in 2007 to 4.4 million barrels a day by 2035 (DOE, 2010). The International Energy Agency (IEA), in its Blue Map Scenario, predicts the increase of biofuel energy production as well as land use as far out as 2050 (See Figure 2.1) (International Energy Agency [IEA], 2008). The IEA compares biofuel production of first- and second-generation biofuels in terms of production and land use. Biodiesel is expected to account for about 50% of energy provided by bio-based liquid fuels by 2035 and near 70% by 2050.

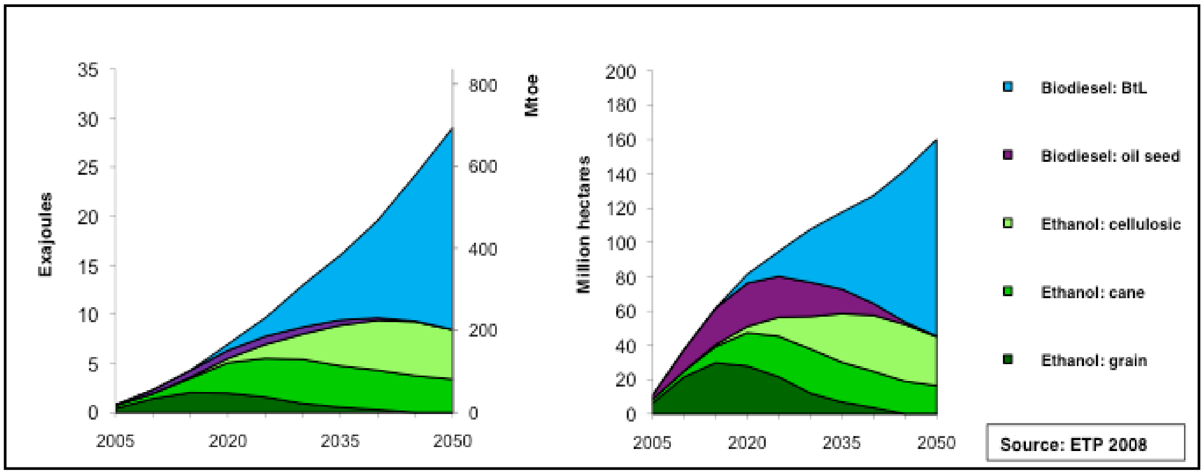


Figure 2.1 A forecast for biofuels : Projected biofuel energy production (left) and projected land use for biofuels (right).

Note. Adapted from "Energy Technology Perspectives 2008, Figure 9.12" by the International Energy Agency, p. 338.

Global Land Use

Only 2% of global arable land is dedicated to bio-energy crops while 30% of readily arable land is unused (El Bassam, 2010). The earth's land area is estimated to be 13 billion hectares. Total rain-fed arable cropland is estimated at 4 billion hectares. Arable land currently in agricultural use is estimated to be at 1.6 billion hectares. According to the Food and Agriculture Organization (FAO), global arable land scarcity is not a problem (Organization for Economic Co-operation and Development [OECD] & Food and Agriculture Organization [FAO], 2007). Less that 20 million hectares are presently used for the biofuels industry collectively, compared to the 5000 million in use for crop and pasture land (International Energy Agency [IEA], 2007). However, global land availability does not necessarily translate to regional security where issues such as water resources, soil quality, and weather can affect food more generally crop production (El Bassam, 2010).

Energy Inputs for Agricultural Production in Developed and Developing Nations

Studies were conducted in the mid 1990s comparing fossil energy inputs per hour of agricultural work. Comparisons included fossil energy that went into the production of any operation as well as into its operation. Developed nations used about 85 MJ/h compared to 1 MJ/h in developing countries. Much of the energy expenditure for developed nations lay in the mechanization of monocultures characteristic of industrialized agriculture. Developing nations, on the other hand, tended to grow several crops side by side without large-scale mechanization, yet the input of fossil inputs for fertilizer and irrigation was higher at 7.4 GJ/ha versus 4.9 GJ/ha in developed nations. Workers in developed countries were able to cultivate 12 hectares per person per year while a single individual in a developing nation managed to cultivate only one hectare per year due to lack of equipment and other inputs. However, developing nations were more efficient at producing food per hectare. Per-farmer output in developing countries was 24.2 GJ/ha compared to the developed country worker who managed to harvest 10.1 GJ/ha, an output ratio of 1:2.4 compared to the energy input ratio of 1:12 (Giampietro & Mayumi, 2009).

Food Versus Fuel

The complexity of the food versus fuel issue is dependent on “changing diets, urbanization, expanding populations, flawed trade policies, extreme weather conditions and speculation” (p.12) (El Bassam, 2010). Biofuel production is essentially an extension of agricultural production, using many of the same resources. There is concern that fuel production displaces food production and increases world hunger. Food price spikes in 2007 in conjunction with a growing agro-fuel industry led to the conclusion that biofuels were the cause of increased market prices (Lederer, 2007). Bio-ethanol production in the European Union (EU) and the United States (US) is based on wheat and maize, respectively, both of which are important staple food crops. El Bassam points out in his recently published *Handbook of Bioenergy Crops* (2010) that, after adjusting for inflation, real-world prices of wheat in 1995 and 1996 were 15% higher than the highest price spike of 2007, while ethanol from wheat production in the EU did not begin in earnest until 2003. In the mid 1990s there was no biofuel industry competing for food supply and inflating prices, yet food prices still rose. Some of the problems in the world agricultural markets are structural, while others are random or cyclical (El Bassam, 2010). The economic climate that drove the development of bio-energy crops is the same force that increased the cost of food production: The cost of crude oil prices rose well above $100 a barrel. This increased the cost of food production and was a strong impetus for an already growing agro-fuel industry to invest in new liquid fuel facilities; it also encouraged research and development into second-generation energy crops. In developing countries the limited supply of energy for farming systems has been a central problem regarding productivity. This has further entrenched poverty and, in particular, has increased hunger (El Bassam, 2010) .

Industrial scale agricultural practices have literally changed the landscape, as in the case of oil palm in Malaysia and Indonesia. However, this development was not driven by global fuel demand but by the food, soap, and cosmetic industries well before biofuels came into play. Despite being the world's highest-producing oil crop per hectare, palm only accounts for 10% of the world biodiesel market. According to the World Wildlife

Foundation, 50% of the items on supermarket shelves in developing countries contain palm oil or some derivative (The Economist, 2010). The price of palm oil dropped from $1,250/ton in March of 2008 to $480/ton in November of the same year. Similar trends were noticed in other edible oils (El Bassam, 2010). At first glance it would appear that supply has exceeded demand for vegetable oil, with increased production and lower prices. However, under closer scrutiny similar price fluctuations were evident across other agricultural commodity markets (El Bassam, 2010). It is notable that when vegetable oil prices were elevated the biodiesel industry was in full swing and the industry was lucrative even though 70% to 80% of production cost for biodiesel was frequently attributed to the cost of feedstock (Demirbas, 2009; Worldwatch Institute, 2007). Now that vegetable oil prices have dropped to about a third of their former high levels, many biodiesel production facilities are struggling or have already failed. The biodiesel industry is not primarily dependent on vegetable oil prices, nor is biodiesel demand the primary source behind an increase in vegetable oil and food prices. Agricultural commodities, edible or not, are tied to the price of energy inputs required to cultivate, harvest, process, and transport goods to market. This is true of biofuel crops as well as other non-food crops like the 15 million hectares of coffee and tea that do little to alleviate hunger (El Bassam, 2010).

Cautions and Response to Biodiesel Production

The climate within which biofuels are being developed must be viewed with a measure of caution due to the complexity of the social, economic, and environmental factors that are involved. Problems endemic in modern industrial agriculture should not be adopted in the production of biofuel crops, but hopefully will be changed. Members of the biofuels industry understand the arguments that can be waged against large-scale conversion of arable land to growth of non-food crops. The response that has assuaged some of the protest against biofuel feedstock production has been that these non-food crops can be cultivated on marginal land, thus avoiding a forced choice between food production and fuel production. For example, jatropha has received considerable attention because it provides quality oil, the oil is inedible, the crop can grow on marginal land, it is relatively easy to cultivate, and has the potential to out-produce oil palm. This approach does two things for the biofuels industry. First, it improves public perception of the benefits of biofuel crops. Secondly, it secures a supply of oil for the biofuels industry that the food market cannot affect, thus separating the two vegetable oil markets. Measures that can reduce the loss of food production capacity while promoting growth of non-food biofuel feedstocks are important for fuel and food security, as well as for the future of the biofuels industry.

Biomass Energy and Energy Conversion

Today's energy supply comes from three types of sources: fissile, fossil, and renewable (Demirbas, 2009). Nuclear power and fossil resources are finite, while renewable energy resources are dependent in one way or another on energy captured from the sun (El Bassam, 2010). Biofuels, and in particular biodiesel, are at the end of a very long energy capture and conversion process that begins with photosynthesis. Although solar energy is free it is helpful to put in perspective the process and efficiencies that are incorporated in the production of the feedstock for biodiesel. As an example, the oil palm is the number one oil crop in production today. The crop has an estimated yield of five metric tons of oil per hectare per year. Oil palm has an energy density of 37.8 MJ/kg so that the crop's energy yield is about 189,000 MJ/ha per year. This is equivalent to 0.003% of the average annual solar energy that hits a hectare of land in a year.

Photosynthesis

In terms of energy, photosynthesis is a process that converts solar energy into biomass. The sun delivers a relatively constant supply of solar energy to the earth. This has been measured above the earth's atmosphere to be 1.367 kW/m^2. The earth's surface does not experience the full power of the solar constant due to atmospheric interference. Global location and period of the year are also factors (The German Solar Society, 2009). The average solar energy that does hit the earth's surface per hectare over the course of a year is equivalent to the average amount received per hectare at 40° latitude. At that latitude a hectare is exposed to an average of 1,708,466 kWh of solar radiation over the course of a year. If dry woody biomass has an energy density of 54 kWh/kg and the average solar energy were completely converted into woody carbohydrates, 30,000 metric tons of dry biomass would be produced per hectare, but this does not happen (El Bassam, 2010). In terms of vegetable oil this would equal about 17,600 metric tons of oil per hectare assuming a specific heating value of 97kWh/kg and 100% conversion of solar energy to vegetable oil.

Limiting Factors Specific to Photosynthesis

Photosynthesis is limited to the range of light between 400 nm and 700 nm—essentially the visible spectrum. This range of light represents 43% of total solar radiation. Of this 43%, a maximum of 15.8% can be absorbed; this is the upper limit for absorption of solar radiation by plants. The photosynthetic apparatus itself is only 30% efficient at converting absorbed light into carbohydrates. This means that just over 2% of solar energy that hits a given plant-covered area is converted into biomass (El Bassam, 2010). Given the total solar energy mentioned above, then, we should produce 34,821 kWh/ha per year. If 2% of average solar energy was converted completely to mass or liquid we would expect a yield of 644 t/ha of dry matter, or 352 t/ha of vegetable oil. However, a substantial amount of energy is used for plant processes and is allocated to biological infrastructure in crops. In reality, the highest annual biomass crop production is considered exceptional at around 25 t/ha, while the highest yielding commercial oil crop is oil palm, producing 4-7 t/ha of oil (El Bassam, 2010).

Limiting Factors Pertaining to Agricultural Crop Yields

Light is a primary factor for plant growth but production is frequently limited to growing seasons and contingent on other environmental factors such as soil quality and water availability. Plant genetics and physical structure of a crop have a lot to do with overall efficiency in terms of process as well as land use. Crop density, which can increase the overall efficiency per land area, is dependent on the plant's physical structure, genetic make-up, and favorable environment. These factors are a primary advantage of aquatic energy crops such as algae where plants can essentially be moved for optimal growth. While oil yields for algae are estimated at 7-31 times greater than oil palm, algae has not been established as an energy crop due to complications in production (Demirbas & Demirbas, 2011).

Biomass Energy Conversion Methods and Efficiencies

Energy from biomass can be converted to usable energy by three methods. The primary method used is direct combust of biomass to produce heat, electricity, or a combination of the two. The second method is to produce gaseous fuels such as methane, hydrogen, and carbon monoxide. This fuel can then be directly combusted or used for synthesis of other fuels. The third method is to produce liquid fuels such as ethanol and biodiesel (Demirbas, 2009). As with most energy conversion technologies there are economies of scale, but certain technologies are intrinsically better at converting fuels into usable heat or power. Potential efficiencies are reported to approach 90% for larger (1-20 MWe) combined heat and power plants, and to be as low as 10% for on-site production of electricity using internal combustion engines (El Bassam, 2010). Diesel engines, or more precisely the diesel cycle, have a theoretical efficiency of 56% (Nave, 2005). In reality the efficiency hovers around the mid 45% and varies based on engine type, system, and operational conditions (Wikipedia, 2010).

Safou (*Dacryodes edulis*)

Formal Domestication of Safou

Safou has been a fixture in western and central African agriculture for some time. In 1992, the first tropical tree domestication conference held in Edinburgh indentified certain criteria for identifying trees with potential characteristics that would recommend them for further domestication. The World Agroforestry Centre (ICRAF) led exercises to identify species that warranted further development. *Dacryodes edulis,* or Safou, was one of the fruits identified. Since that time considerable research and effort have been invested in quantifying, characterizing, and developing Safou as a crop for agroforestry systems (Tchoundjeu et al., 2008).

Range of *Dacryodes edulis*

Dacryodes edulis belongs to the family Burseraceae and is indigenous to West Africa. It is found from Sierra Leone down to Angola, and to the east as far as Uganda (El Bassam, 1998). The genus *Dacryodes* contains 34 species, two found in tropical South America, 19 in Africa, and 13 species in the Malaysian Archipelago (International Centre for Underutilized Crops, 2001). The two most recent discoveries were reported in 1996 (Pierlot, 1996). Not all of the species produce an edible fruit but the majority do, and the quality of the wood has made these trees valuable as a source for lumber. However, the fruiting trees are considered the most valuable.

Safou Fruit

The fruit is widely eaten throughout the Gulf of Guinea region and has myriad names, the most common being *Safou* (pronounced să-fu) in Francophone areas, and *African pear* or *plum* in Anglophone areas. Another common name is the butter fruit, which is a reference to the oily pulp which has been shown to have an oil content ranging anywhere from 30-70% of dried pulp weight (El Bassam, 1998). The fruit itself is, on average, about 4-15 cm long and 3-6 cm in diameter. The unripe fruit starts as a rosy pink and moves toward a dark purple as it ripens. A layer of edible pulp, about 1 cm thick, accounts for about half the fruit’s wet weight. This pulp can come in several colors ranging from light pinks to yellows and greens, and it varies in flavor depending on the tree (El Bassam, 1998). Traditionally, the fruit can be eaten raw, poached, boiled, or roasted, but packaged products such as chips and spreads are being produced (Atanga, Bella-Manga, Talle, & Lewis, 2008). Exudates or resins from the fruit stem and tree are used in traditional medicine, and have potential as a raw material for pharmaceuticals. Resin is used to treat against parasites and is valued for aromatic qualities when burnt (Okwu & Nnamdi, 2008).

Market & Crop Developments

The fruit's popularity as a food has helped develop national markets and international markets as far away as Europe (Awono, Ndoye, Schreckenberg, Tabuna, & Isseri, 2002). However, quantifying the value of the entire market has proven difficult, except in localized markets. It is clear that the fruit is at the center of a lucrative and budding trade (Tchoundjeu, Kengue, & Leakey, 2002). Market growth has continued despite an estimated 40-50% loss in fruit post-harvest. These losses are primarily attributed to the fruit's rapid deterioration after harvesting, and to damage incurred during transport of the fruit. Proper harvesting and storage techniques have been identified to extend shelf life, but the narrow window of time available from harvest to market still remains an obstacle (Silou et al., 2006). The fruit's potential has led to further research to identify and selectively breed for favorable tree and fruit traits (Atanga et al., 2008). This research has helped to identify favorable strains and to quantify the tree's oil-producing capacity. A program to isolate favorable traits has led to the identification and cultivation of several varieties for commercial markets. Of the fruit varieties considered, 90% are suggested for oil extraction (Atanga et al., 2008). Due to the oil's quality and the potential forproduction, oil extracted from the pulp has been suggested as a non-traditional oil feedstock for the food and cosmetic industries (Atanga et al., 2008; El Bassam, 1998).

Oil Production Capacity

Dacryodes edulis has only recently been selected for domestication and cultivation. Assuming the present yield capacity of trees Safou can produce as much oil as the cultivated oil palm which has enjoyed a century of selective breeding (National Research Council, 2008). This amounts to 4-6 tons/ha. However, it has been reported that some tree strains have the potential to producing 10-15 t/ha, assuming organized cultivation and ideal growing conditions. This is more than twice the volume of which the cultivated oil palm is capable. Unlike the oil palm, where pulp and kernel have significantly different oil, the oil present in the pulp and kernel of the Safou fruit is very similar. This characteristic has the potential to make harvesting the oil simpler and consequently more economical (El Bassam, 1998).

Oil Appearance

Raw Safou oil has an olive green color, is semi-solid at room temperature (Dzondo-Gadet, Nzikou, Matouba, Etoumongo, Linder, & Desobry, 2005), and frequently separates into two layers: a liquid upper and a semi-solid bottom layer (Obasi & Okolie, 1993). The presence of the greenish hue is suggested to be due to the presence of chlorophyll pigments. Once bleached and degummed, the oil has a yellowish-brown coloring (Arisa & Aworh, 2008).

Characteristics of Pulp and Seed Oil

Fatty acid composition. Biodiesel is formed by attaching an alcohol to fatty acids. The nature of the feedstock's fatty acid composition has direct bearing on the characteristics of the fuel made. Safou pulp and seed oil are made up primarily of three fatty acids that generally account for 95% of the total fatty acids. The pulp oil includes palmitic acid (C16:0; 35.6 to 58.4%), oleic acid (C18:1; 16.9 to 35.5%), and linoleic acid (C18:2; 3.9 to 31.5%) (El Bassam, 1998). This means that Safou pulp oil is composed of approximately 50% saturated, 25% monounsaturated, and 25% polyunsaturated fat content. This composition tends to make the oil stable even at high temperatures (Dzondo-Gadet, Nzikou, Matouba et al., 2005). The presence of saturated molecules has been correlated to lower NOx emissions. Conversely, the increased number of double bonds in unsaturated fatty acids correlates to increased flame temperatures during combustion and consequently to higher NOx emissions (Sun, Caton, & Jacobs, 2010).

Melting points. Safou's primary melting point is at 14.5° C, more than 10°C lower than coconut and palm oil, which have major melting points at 25°C. This would suggest that Safou oil has a lower cloud and gel point than biodiesel made from coconut or palm oil. This lower primary melting point is due to a larger fraction of fatty acids with shorter chain lengths in comparison to palm or coconut oils (Dzondo-Gadet, Nzikou, Matouba et al., 2005). Safou pulp oil does present three distinct melting points if thawed from a below-freezing temperature. These three melting points are directly correlated to its three main constituent triglycerides. For purposes of separation of these triglycerides from one another, cooling the oil to a specific temperature and then centrifuging it can separate larger fatty acids from the smaller ones. Table 2.1 provides a comparison of Safou with various other oils.

Table 2.1

Composition by Percentage (%) of Saturated and Unsaturated fatty Acid in Major Oils

Seed or fruit	**Carbon number**							
	C14	**C16.0**	**C16.1**	**C18.0**	**C18.1**	**C18.2**	**C18.3**	**C20**
Peanut (USA)	0.04	10.6	0.13	2.41	47.05	30.77	0.14	1.31
Colza- Canola		5.56	0.12	1.38	58.25	22.17	8.9	0.22
Sunflower		6.27		4.86	19.69	67.44	0.03	0.31
Olive		14.31	1.65	2.48	66.68	13.91	0.5	
Soybean		11.03		3.91	23.04	56.84	7.9	
Maize		10.69	0.12	2	25.46	59.35	0.92	0.37
Palm	0.89	43.14	0.18	5.41	38.72	10.59	0.27	0.39
Safou		42.4±0.4	0.2 ±0.1	2.5±0.1	27.8± 0.45	25.2±0.1	1.2± 0.5	

Note. Adapted from "Characteristics and nutritional interest of safou pulp oil" by Dzondo-Gadet et al. ,2005 in Process Biochemistry. 40,p.?

Viscosity and saponification values of Safou oil. The ratio of saturated fatty acids to unsaturated fatty acids in Safou pulp oil is reported as being close to 1:1, which is similar to palm oil. This value places it between fluid oils at R=4 and vegetable butters at R=0.25 (El Bassam, 1998). The oil's viscosity decreases rapidly above 10° C. When compared to oil palm, the viscosity of Safou oil is half as much at 25° C (Dzondo-Gadet, Nzikou, Matouba et al., 2005). Saponification values of raw oil were established by Arisa and Aworh (2008) to be 217.39 +/- 0.318. This figure dropped substantially to 57.08 +/- .060 after degumming with 5% NaOH and bleaching (Arisa & Aworh, 2008). Viscosity, saponification values, and degumming characteristics have bearing on the fuel production in terms of the oil's processing, storage, and fuel production characteristics.

Seed oil. The seed oil characteristics are similar to, but not entirely like, the pulp oil characteristics. This has bearing on the efficiency of oil extraction and consequently on the energy balance of biodiesel made from the Safou fruit. As with the pulp oil, the seed oil does separate into upper and lower layers, similarly to the pulp oil, but the saponification value is lower (173-179), correlating to a slightly greater presence of unsaturated (palmitic acid) chains. The seed oil also has a low iodine value, which is said to make it less prone to oxidative rancidity (Obasi & Okolie, 1993). Beginning with a raw oil with low iodine value translates into higher biodiesel yields assuming a base catalyzed reaction common to biodiesel production. The specific gravity of raw seed oil was reported by Arisa and Aworh (2008) to be 0.9131, similar to that of pulp oil. Arisa and Aworth also reported a lower specific gravity after bleaching. The specific gravity of saturated or unsaturated oils has bearing on the measure yield in terms of initial volume and final fuel volume. This is generally explained by losses to free fatty acids which drop out with the glycerin fraction (see Table 2.2).

Table 2.2
Characteristics of the Fixed Oil of the Seeds and Fruit Pulp of Dacryodes edulis

	Seed	**Fruit pulp**[a]
Free fatty acids	7.3	14.1
Saponification value	173.9	201.4
Iodine value	8.8	59.6
Specific gravity	0.843	0.9
Non saponifiable matter	1	
Fatty acids (%)		
Palmitic	61.9	47.89
Oleic	18.3	31.25
Linoleic	19	17.5

[a]After Omoti and Okiy (1987)
Note. Adapted from “Nutritional constituents of the seeds of the African pear, *Dacryodes edulis”*.by O. N. Bonkens and O. N. Paulinus.1992.. *Food Chemistry*, p. 297-299.

Processing Safou for Oil Extraction

Drying. Oil has been extracted from the pulp and kernel of Safou in several ways. For most oil expression methods drying the fruit to less than 10% water weight prior to extraction was essential, with the use of enzymes as mentioned offering the exception. Initial water content is about 60-70% of the fresh pulp's weight. Two drying methods were compared in one study. Solar dryers reduced the fruit moisture content from 70% to 13% in five days. An electric dryer reduced moisture content from 57% to 7% in just 15 hours (Kapseu, Avouampo, & Djeumako, 2002).

Chemical oil extraction. Chemical extraction was successful with the use of hexane after the pulp or kernel was dried and crushed (Dzondo-Gadet, Nzikou, Etoumongo, Linder, & Desobry, 2005). Hexane achieved a near total extraction. In other instances, the Bligh and Dyer method was used, which uses a solution of methanol and chloroform in ratios of 2:1 by volume. This method is much faster than the use of hexane but is not necessarily as efficient in extracting the total lipid content from the fruit.

Enzymatic oil extraction. The use of enzymes has also been tested in the extraction of oil from Safou pulp and seeds. This method does not require drying. Using the enzyme Viscozyme L. achieved extraction rates no less than 2% below percentages achieved with the Bligh and Dyer method. This is promising for applications in extracting oil for food purposes (Dzondo-Gadet, Nzikou, Matouba et al., 2005).

Mechanical oil expression. The screw press method of oil removal was done by drying the fruit pulp and seed and using a screw-press. This method is not as efficient as chemical extraction processes but is less expensive and requires less infrastructure and technical expertise. Oil extraction as a percentage of dry weight was reported at 25-40% for an electric press and at 23-28% for a manual press (Kapseu, Avouampo, & Djeumako, 2002). The specific press models were not mentioned. The residual oil cake from oil pressing, which has a protein content between 13-16%, can be used as an animal and fish food (Silou et al., 2006). Table 2.3 provides a comparison of these extraction methods.

Table 2.3
Process and oil rate extraction

Process	Press		Solvent		Enzyme	
	manual[a]	electric[a]	(Bligh/Dyer)	(Soxhelt)	Neutrase	Viscozym L
Extraction level (% of oil)		34.8 ±0.38	43.2±0.5	47.0 ±0.1	28 ±0.9	42 ±0.7

Note. Adapted from "Post-harvest losses by natural softening of safou pulp (Dacryodes edulis) in Congo-Brazzaville" by T. Silou, D. Massamb, J. G. Maniongui, G. Maloumbi & S. Biyoko, 2006. *Journal of Food Engineering, 79,* p. 392-400.

Nutritional Value of Safou Fruit

Safou makes a positive contribution to the lives of both producers and consumers. The Safou trade significantly impacts the livelihood of both farmers and merchants, financially as well as nutritionally. The fruits nutritional make up is summarized in Tables 2.4 – 2.6. The tree provides food and a source of income prior to the harvest of staple food crops at a point when financial means are nearly exhausted. It also provides other necessary resources like wood (Atanga, Bella-Manga, Talle, & Lewis, 2008). As a food, the high concentration of polyunsaturated fatty acids in the fruit aid in reducing coronary heart disease. A positive correlation between Safou consumption and improved quality of breast milk has also been reported (Dzondo-Gadet, Nzikou, Matouba, Etoumongo, Linder, & Desobry, 2005).

Table 2.4

Proximate Composition of the Seeds and Fruit Pulp of Dacryodes edulis *(g/kg^{-1} DW)*

	Seeds[a]	**Fruit Pulp**[b]
Carbohydrate	7.6 ± 0.91	135
Protein (N x 6.25)	338 ± 4.38	259
Oil	120 ± 3.74	319
Energy (kcals/kg^{-1})	2736 ± 35.69	4447
Ash	126 ± 2.27	108
Fibre	173 ± 2.52	179

[a]Mean of four determinations ± SE
[b]After Omoti & Oky (1987)

Note. Adapted from "Nutritional constituents of the seeds of the African pear, *Dacryodes edulis"*.by O. N. Bonkens and O. N. Paulinus.1992.. *Food Chemistry*, ,p. 297-299.

Table 2.5

Mineral Composition of Dacryodes edulis' Seeds
(g/kg^{-1} DW)

Mineral	**Content**
K	23.94
Ca	7.3
Mg	10.8
Zn	0.36
P	2.18
Cu	0.05

Note. Adapted from "Nutritional constituents of the seeds of the African pear, *acryodes edulis"*.by O. N. Bonkens and O. N. Paulinus.1992.. *Food emistry*, ,p. 297-299.

Table 2.6

Amino Acid Composition of Dacryodes edulis' Seeds

(% total amino acids)

Amino acid	**Content**
Essential	
Lysine	8.41
Phenylalanine	4.97
Leucine	18.56
Isoleucine	7.5
Methionine	0.94
Valine	3.45
Arginine	2.9
Non-essential	
Aspartie	13.08
Serine	4.49
Glutamie	12.02
Proline	5.72
Glycine	2.29
Alanine	7.12
Tyrosine	4.52

Note. Adapted from "Nutritional constituents of the seeds of the African pear, *Dacryodes edulis".*by O. N. Bonkens and O. N. Paulinus.1992.. *Food Chemistry*, ,p. 297-299.

Safou's Contribution to Oil Crop Diversity

Propagation of *Dacryodes edulis* as a crop increases the diversity of highly productive vegetable oil species in the tropics (El Bassam, 1998). The tree is native to the tropical regions of western and central Africa. It has more to offer overall than the oil palm, as a shade tree, for firewood, and for timber. It also works well in multiple-crop agroforestry systems (Aiyelaagbe, Adeola, Poppola, & Obisesan, 1998). It thrives in acidic soils where land tends not to be as fertile and is a significant supplement to fat and protein poor diets. Essentially, the Safou tree enhances the security of food supplies (El Bassam, 1998).

Genetic Obstacles to Propagation of Safou

Morphological obstacles. *Dacryodes edulis* demonstrates a high tree-to-tree variation in fruit traits, including size, shape, skin and pulp color, pulp thickness, taste, and shelf life. This complicates matching product to market desires. Selection of fruit types has not been fully developed or fully implemented to meet quantity and quality consumer demands (Atanga et al., 2008). Safou trade continues to grow but has not gained full momentum largely because of the tree's genetic variability.

Gender selection in propagation. The species is composed of male and female trees but can display hermaphroditic traits. It is also suspected of selecting gender during maturation. The natural ratio of male to female trees tends to be 1:1, and tree sex cannot be identified until well into growth, complicating efforts for orchard development to maximize fruit harvests. Maturation of trees grown from seedlings has been reported to occur after 4 to 5 years at the earliest (Aiyelaagbe et al., 1998). Seeds from trees that have favorable traits do not necessarily retain parent tree traits. These characteristics have implications for propagation and crop development.

Propagation techniques. Aerial layering, a process where clones are created by cultivating branches off of adult plants, has shown to result in trees that retain a donor or parent tree's favorable traits. Using this method, planted clones can begin fruiting within 18 months. However, this method removes branches from a host tree and the total generation is limited to the number of favorable branches on the host (Atanga et al., 2008). The fruit's genetic variability could prove to be an advantage in developing fruit varieties that are inedible but that have high oil content. It may be possible to develop different Safou cultivars with various end uses, either for fruit or for oil production.

Harvesting Methods and Socio-Economic Considerations

There appears to be a human-gender-specific division of the labor associated with Safou fruit harvesting. Taking fruit from the tree, depending on its height, is accomplished by climbing the tree or knocking it down with a pole, work that is largely done by children or men. Women and children gather the fallen fruit, and women are responsible for transporting and marketing the fruit (Schreckenberg, Degrande, & Mbosso, 2002). The harvest of Safou in Cameroon tends to occur prior to other primary crop harvests and provides a source of money when household income is low and school fees are due due (Schreckenberg et al., 2002). At present, the structure of the Safou trade is such that men and heads of households own trees while the women are primarily in charge of the trade both at the village level and at the point of sale to consumers. As Safou becomes a cash crop, there are worries that women will be by-passed by wholesale merchants who tend to be men and who bring their own laborers to harvest entire trees (Schreckenberg et al., 2002).

Harvesting Considerations

Timing of harvest. Timing for the harvesting of fruit crops is subject to two criteria: The fruit's physiological maturity and its commercial maturity. Physiological maturity is the progression of the fruit's developmental stages that culminate in the fruit's senescence, or the point at which it begins to deteriorate or decay. Commercial maturity is whichever point of physiological maturity that matches infrastructure and market demand. Harvesting methods also depend on the characteristics of the crop. Methods are usually aimed at minimizing damage and decay (Ingram, Vince-Prue, & Gregory, 2008). Safou fruit maturation is indicated primarily by color and senescence is indicated by a change in fruit firmness. In the case of Safou for oil production, harvesting would optimally be done at the point of senescence, since oil content is suspected to increase with duration of maturation on the tree (Kinkéla, Kama-Niamayoua, Mampouya, & Silou, 2006)

Period of harvest. Safou is found above and below the equator, and consequently the fruiting season is almost year-round. The fruits begin to ripen in early January and can be available until late May in the D.R. Congo; in Cameroon, Safou fruit begins to ripen in May and is still available in early October (Isseri & Temple, 2002). Though no information was found for the growing season for Safou in Angola, it is reasonable to assume that there could be a crop available in various African locations nearly year-round. Fruit tend to present all at once in loose clusters, but maturation of the individual fruit occurs individually over time.

Harvest challenges. Harvesting Safou poses some challenges. The determination for the correct time to pick a fruit is difficult to gauge, particularly when large quantities are being harvested. Within horticultural practice, the most reliable method to gauge and predict fruit ripeness is degree-days or heat units, in addition to color, fragrance, or softening. Using these methods and indicators, particularly in controlled greenhouses, commercial crop maturity can be precisely orchestrated (Poincelot, 2004).

Mechanization of harvest. Many methods of mechanized and semi-mechanized harvesting have been developed for various fruit tree crops. Harvesting equipment has also been successfully developed for fruits that are easily bruised. The efficiency of mechanized harvesting is, however, dependent on plant breeders developing cultivars with physical traits and ripening traits that aid in harvest (Poincelot, 2004). The introduction of aerial layering where branches are transplanted into the ground has produced clone trees that remain close to the ground. This development has aided in manual harvesting and would be essential to mechanization providing a smaller tree that can either be shaken or the fruit knocked off with market ready machines.

Post-harvest treatments. After a fruit is picked it is still a living organism with biochemical physiology that affects quality, flavor, and texture (Poincelot, 2004). With Safou fruit, maturation and decay is primarily attributed to the action of pectin on the cellular level (Missang, Renard, Baron, & Drilleau, 2002). After fruit is picked, respiration continues, whereby metabolic processes in the mitochondria oxidize sugars, releasing heat and CO_2, and, in some cases, the process is anaerobic (Ingram et al., 2008). The short shelf life of Safou fruit has prompted the use of airing the fruit and the investigation of wax coatings and cold storage to improve shelf life. The most common method for transport of Safou is in 50 kg mesh sacks that allow the fruit to breath. Close proximity of the fruit increases the fruit temperatures and perspiration or condensation on the fruit.

Safou Processing Considerations

End-Use Requirements

The method of processing Safou in order to remove the pulp is dependent on the purpose for the pulp and, in the case of oil extraction, the quality required for a given market. For food pastes and spreads only the pulp is useful, which requires separating pulp from the thin skin and central seed cluster. This poses significant complexity for industrial-scale processing and mechanization. If Safou is destined for oil production the pulp provides the highest yield; however, seed oil is similar in nature to pulp oil and does not necessarily need to be segregated.

Physical Properties

Mechanization considerations. The pulp of Safou can be firm enough to require mechanical separation of pulp from the seeds' cluster, or soft enough that the pulp can be washed off. Mechanized de-pulpers, decorticators, and de-stoners are market-ready for small-scale fruit processing applications in developing country situations (Intermediate Technology Development Group, 1992). These machines could be modified for application in safou pulp and seed removal, however there is no standard mechanization for this processes. Market and end product dictate process and at present safou production is primarily a fresh fruit industry.

Water separation. When Safou pulp is still firm it floats, but the seed center will sink if the membrane around the cluster is sufficiently ruptured for trapped air to escape. On the other hand, fruit pulp that is sufficiently softened will come off of the central seed cluster and pouch and sink while the intact cluster will float. The potential for water separation of the pulp is possible in either scenario. However, the advantages gained through water separation would have to be weighed against the energy needs of subsequent processes.

Drying Safou Fruit Pulp

Introduction

The method of oil removal used for the samples in this research required the drying of Safou fruit pulp. Understanding the drying process was essential to this research for three reasons. First, the drying process has bearing on the quality of the oil and potentially the biodiesel end product. Secondly, it informs us of the general process demands for further development. Thirdly, this intermediary process has considerable energy balance implications and understanding it is essential to evaluating the overall process and Safou's potential as an energy crop. All three of these reasons encompass issues of quality, energy, and potential and are essential to understanding the fruit's viability as a biofuel feedstock.

Drying Background

The goal of fruit drying is to remove water; this is most commonly done with heat and convective air (Jayaraman & Das Gupta, 1992). Fruit samples are placed in an oven at temperatures between 70-105° C and monitored for weight change. A zero point is achieved when weight reduction ceases (Karathanos, 1999). Once a zero point is established, monitoring the weight change of the sample informs the moisture percentage based on weight. One of the primary objectives of food drying is to convert a perishable item into a stabilized product that can be stored for extended periods (McMinn & Magee, 1999). In addition, food drying can enhance quality, increase ease of handling, conserve energy in subsequent processes, reduce the cost for transport, and prepare material for secondary processing (Sokhansanj & Jayas, 1995).

Food Drying Kinetics

Moving water out as efficiently as possible with minimal energy requires managing several changing interactions. Moisture diffusivity, thermal conductivity, density, specific heat, inter-phase heat, and mass transfer coefficients are some of the primary factors considered when modeling the drying process (Karathanos, 1999). First, it is essential to understand the properties of water and the three primary drying variables including water-water, water-solid, and water-air interactions. Secondly, the drying process, in which all three variables are fluctuating, can be understood in terms of initial drying dynamics and terminal drying dynamics. The upshot is that removing a pound of water from food matter is not as straightforward as boiling off a pound of water. Drying foodstuff requires more energy because water must overcome not only water-water bonds but also water-solid bonds with the vegetable material. Furthermore, water must travel from inside fruit structure to the exterior, which also requires energy. In short, the primary elements involved in drying fruit pulp include the nature of the moisture and the changing drying dynamics.

Free and bound moisture. Water in fruit is considered to be either "free" or "bound" moisture. Free water resides in the interstitial spaces and pores and is held by physical forces related to surface tension. This moisture content behaves similarly to pure-liquid water. The bound fraction, which is sorbent or solute-associated water, presents kinetic and thermodynamic properties differing from pure-liquid water. This fraction is held inside and outside of the fruit cell walls by water-solid interactions. This layer forms a monolayer foundation for multi-layer water-water interactions (McMinn & Magee, 1999). These water-solid interactions require additional energy to overcome compared to water-water bonds.

Initial drying dynamics. During drying the free water evacuates the cells, making its way through the cellular capillaries to the surface. Initially this causes structural shrinkage that ceases before drying is complete (Brennan, Butters, Cowell, & Lilley, 1990). At this point there are voids and hollows in the cell structure, which decrease thermal transfer. Thermal conductivity in foods is primarily dependent on chemical composition of aqueous constituents. The presence of oil in cellular structures inhibits the flow of moisture because of the oil's hydrophobic nature (McMinn & Magee, 1999).

Terminal drying dynamics. Once the structural shrinkage ceases, the drying of the remaining water fraction is affected more by the physical properties of the vegetable material. These properties include fiber orientation and solid thermal properties. How the water migration is controlled as it moves toward the surface has a direct bearing on the characteristics of the material that is left behind (McMinn & Magee, 1999). In other words, if the temperature during drying is elevated to force vaporization of the water content it may cause structural degradation at the cellular level. The material of cell structures may not be affected by boiling temperatures; however, the boiling water can physically affect the plant structure. Towards the end of drying there are more interstitial spaces to accommodate the evaporation of moisture so that elevating temperatures toward to the end of the drying process is favorable in terms of removing moisture content (McMinn & Magee, 1999). However, this may need to be balanced with the need to preserve the nutrients in organic cells. Elevated temperatures have been observed to cause oil to split, forming free fatty acids; this has direct consequences in terms of processing efficiency (Kundu, 2004).

Drying Curves

While initial and terminal drying dynamics address the general progression toward drying, the entire process as represented with a fruit-drying curve is frequently separated into three phases. The first phase is that of the loosely-bonded water evaporating. This is also known as the *constant drying rate*, in reference to the constant presence of moisture evaporating at the material surface producing a relatively linear drop in weight (Jaturonglumlet & Kiatsiriroat, 2010). The second phase, which represents the last water to go, is termed the *falling rate period* that occurs as the surface dries and evaporative action begins to occur inside the cellular structure. This phase is primarily comprised of evaporation of the monolayer, which is directly attached to surface solids by strong molecular forces. This moisture represents about 3-6% of the weight of the samples (Karathanos, 1999). The last phase, termed the *full falling rate*, refers to when solids begin to evaporate as well (Jayaraman & Das Gupta, 1992). In sugary foodstuffs, for example, fructose begins to break down and evaporate in the full falling rate phase. The absence of a full falling rate can be indicative of an absence of fructose content (Karathanos, 1999).

Air Temperature and Velocity

The transfer of moisture out of a material is primarily dependent on air temperature and secondarily on airflow. Air temperature is an influence during the entire process. Air velocity has great effect while moisture content is high but does little at low moisture content (McMinn & Magee, 1999). In practical solar applications, allowing convection to take place during the initial stages is effective at transporting moisture away. On the other hand, during the last segment of the drying process it is more advantageous to close the system and allow temperatures to rise. An increase in far-infrared radiation directly hitting the media being dried results in shorter drying times (Jaturonglumlet & Kiatsiriroat, 2010). This may explain some differences between the efficiencies of direct and indirect solar drying applications.

Vegetable Oils and Pressing

Overview

Vegetable oils are lipids, which are contained in the cell structure of plant matter. Compromising the cellular structure and liberating the oils is done by orchestrating the mechanical as well as the chemical effects of pressure, temperature, duration under compression, and moisture content. In general, *expression* is a term denoting mechanical removal of oil, while *extraction* refers to chemical removal (Khan & Hanna, 1983). In practice, highest yields incorporate elements of both expression and extraction.

Cold Press

By eliminating the chemical action of heat, cold pressing does not chemically alter the feedstock. The temperature threshold for cold pressing is debated, but 90° F is at the bottom of the debated range. Cold-pressed oil is generally considered more valuable than hot-pressed oils, but cost is also affected by yields and process efficiency (National Sustainable Agriculture Information Service, 2008).

Extraction

Heat, digestion, solvents, and enzymes are all extractive techniques that chemically affect the oil feedstock. Oil content is liberated by action on the cellular structure. Heat denatures and segregates proteins, collapsing cell structures and making oil globules less viscous, thus increasing flow during expression (Khan & Hanna, 1983; Owolarafe & Faborode, 2008). Digestion, heating the feedstock, or allowing it to rot all essentially chemically break down cellular structures as resident enzymes such as pectin metabolize and act on the cellular structure. In the case of solvent extraction, mechanically pre-crushing the feedstock to shear feedstock structures improves yields by increasing surface area on which the solvent can act. Pulverizing feedstock before enzyme application also accelerates the efficiency of extraction. More recent developments using super-critical gasses for mechanical and chemical extraction change the feedstock and are also more efficient when solvents are incorporated (Salgın, 2007).

Expression

The screw press is the most widely used method of vegetable oil extraction (Mrema & McNulty, 1985; Singh & Bargale, 2000). The design of a screw press is a balance of objectives that work against one another. On one hand, compression ruptures cellular structure, allowing oil to flow out; however, compression also collapses the organic structure and can trap oil (Khan & Hanna, 1983). Cellular rupture and the timed collapse of the organic structures in a press require control of moisture content, compression, duration of compression, and heat. If there is too much moisture compression does not occur because the friction coefficient decreases; too little and oil remains in the feedstock and the press may bind-up (Singh & Bargale, 2000). In the case of excessive heat the oil may lacquer, affecting oil quality or sealing in oil, while too little heat slows oil flow. Balancing moisture, heat, compression, and time in the press can be complicated, but managing this balance is essential for efficient extraction.

Balancing Moisture, Heat, and Compression

Moisture. Controlling the moisture content of a feedstock is essential for several reasons. One reason is for storage and long-term stability of the feedstock. Another is to maximize extraction yields. Excess water in the feedstock decreases the friction coefficient by increasing plasticity (Singh & Bargale, 2000). At the other extreme, excessively dry feedstocks exceed the ideal friction coefficient, binding up the press and increasing wear.

The ideal moisture percentage is one that maintains a constant friction, compromises cell structure, and aids in oil flow. The effect of moisture content is specific to each feedstock but as a general rule is ideal around 8% wet weight for typical press conditions (Khan & Hanna, 1983). This percentage is interesting in light of the 3-6% moisture attributed to the monolayer of water that attaches to inter-cellular structures reported by McMinn and Magee (1999). This would suggest that on the cellular level ideal moisture content exceeds the monolayer of water molecules in the press feedstock.

Heat. As press science has progressed, the ability to control heat has improved. Heat may be applied to a feedstock before it is pressed, and additional heat is generated by friction in the press. More recent developments in press design have included the use of heating collars on the press housing. This is more efficient than preheating feedstock and is better suited for maintaining press temperatures. To maximize press extraction, maintaining temperatures above 100° C improves both progression of material through the press and yield. However, it is important to note that excessive heat will also undermine the compression of the feedstock and reduce yield. Energetically it is more efficient to generate heat with a heated collar than to generate that same heat mechanically. Temperatures in excess of 100° C would require significantly more friction, requiring additional power inputs as well as a press design that could accommodate the stress. As mentioned before, high compression does not necessarily correlate to more oil extracted. It is a matter of controlling the progression of compression so that oil may escape.

Heat also affects the structure of the feedstock. It deteriorates the cell structure, changing the physical and chemical characteristics of the material. These effects can be orchestrated with moisture content and with duration of time in the press to help maximize yields. Once the raw oil has been collected it usually undergoes refining, which begins by removing particulates and other impurities. The extent of refining after pressing depends on the oil's final purpose. In the case of biodiesel the oil needs to be dry and free of particulates. Processing the oil by degumming and bleaching is not necessary because much of the material removed during these processes is removed by the transesterification process.

Compression. Compression in a screw press is generated by both axial and radial force (Ward, 1976). A continuous screw press can be conceived of in three compression sections: The feed section, the ram section, and the choke section, see Figure 2.2. At the feed section, radial compression macerates and homogenizes feedstock as it progresses to the ram section. According to Ward (1976), the axial compression must always exceed radial compression forces. In other words, the pressure exerted by the screw along the press is slightly greater than the pressure out against the housing. When radial force exceeds axial force the press either binds up or material finds its way out axially through the press housing and into the oil.

The purpose of compression is to reduce the volume of a feedstock in order to force the oil out. Theoretically, a given feedstock will have a particular compression ratio where all the oil is removed. The peanut, for example, has a theoretical ratio of 4.3:1, where initial peanut volume of 4.3 must be reduced to 1 for complete oil extraction (Singh & Agarwal, 1988). Singh and Argawal define screw-press compression ratios as "the ratio of volume of material displaced per revolution of the shaft at the feed section to the volume displace at the choke section" (p. 77). A common ratio for a screw press is 10:1. This ratio, though well above most theoretical ratios for feedstocks, is necessary to accommodate for slippage and rotation of the feedstock as it is compressed (Singh & Bargale, 2000). Compression can be regulated by pitch of the screw, depth of the channel, and tapering of the screw.

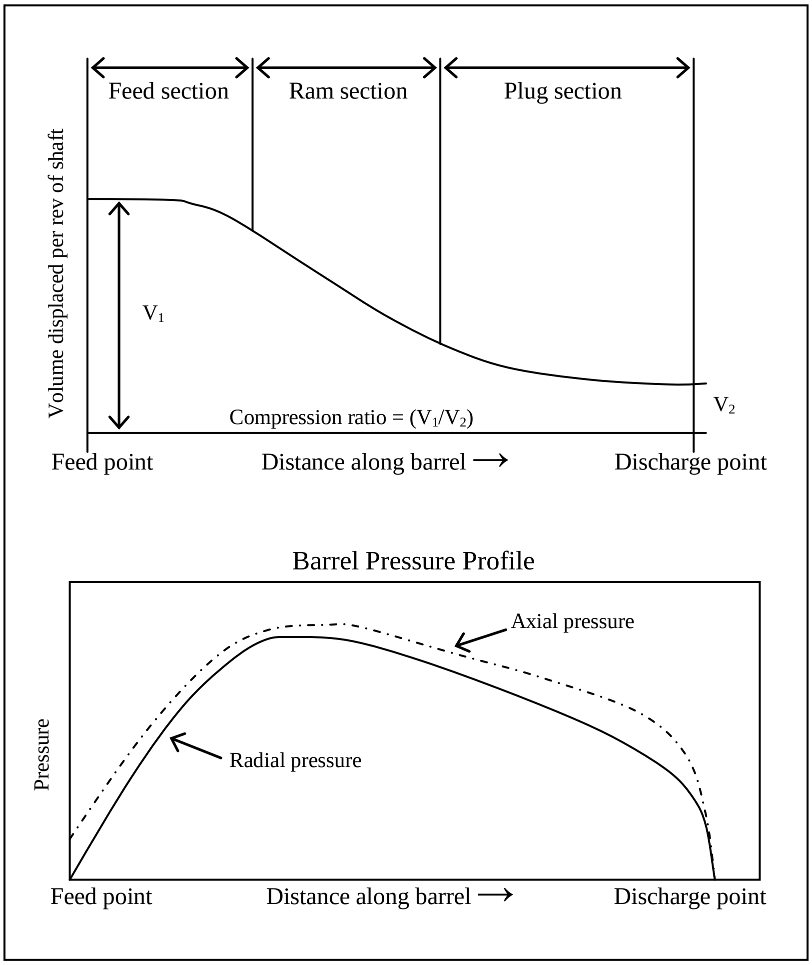


Figure 2.2. Compression curve and barrel pressure profile
Note. Figures adapted from "Expression of Oil from Oilseeds - A review" by L.M. Khan and M.A. Hanna, 1983. *Journal of Agricultural Engineering Resources*, *28*, 495-503.

Screw-Press Advantages and Disadvantages

The primary advantages stated by Singh and Bargale (2000) for screw-press popularity are its simplicity and relative safety, making it more attractive than use of solvent extraction equipment. Another big advantage is that it produces end products that are free of chemicals (Khan & Hanna, 1983). The screw-press has sufficient extraction percentages, usually above 80% of total potential oil yield. The byproduct and meal left after extracting the oil are usually valuable for food additives and livestock feed. The flexibility of being able to modify a press for different feedstock is also an advantage. In developing countries, the sturdy build of a screw-press means it can endure misuse by inexperienced operators and survive until operators better understand press and feedstock control. The increased use of human labor also makes the cost of operation acceptable in relation to market prices for the oil and by-products (Singh & Bargale, 2000).

Disadvantages of the screw-press include the difficulty of controlling feedstock characteristics for optimal extraction. Press set up and clean up can be time consuming and its use only really makes sense when large, continuous runs can be undertaken. At approximately 80%, the typical oil yield does not represent a complete extraction of the oil content. However, oil remaining in the meal can be recuperated either by selling the meal or combusting it for process heat, or simply by composting the material for soil amelioration (Encyclopædia Britannica, 2010).

Press Efficiencies

Oil expression is contingent on feedstock characteristics and their reaction to the forces in the press. Press efficiency can be as high as 90%, but this usually requires multiple passes through the press (Khan & Hanna, 1983). Secondary passes can require less energy in comparison to the first passes with similar oil extraction rates. However, this is not always true as feedstocks become drier and realized compression ratios approach the actual compressibility limit of a feedstock (Singh & Bargale, 2000).

Press energy efficiency calculations are dependent on expression efficiencies and overall yield. Press energy efficiency can then be calculated with energy used per volume of oil expressed. This calculation is an essential part of analyzing biofuel applications.

Biodiesel Production

Biodiesel is a petro-diesel fuel substitute produced from vegetable oils. The process of converting raw oil to usable fuel can take several reaction paths to end up with esters. Esters are formed by combining free fatty acids from triglycerides with an alcohol such as methanol or ethanol to produce fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE) (Gupta & Demirbas, 2010). Industrial production of biodiesel most commonly uses methanol as the alcohol because of its cost and because it has a less hydrophilic nature than ethanol.

Biodiesel Feedstock

Triglycerides. Fats and vegetable oils are triglycerides. Triglycerides are made up of a single glycerol back-bone molecule and three fatty acids of various chain lengths. The triglycerides are the feedstock for most biodiesel produced today, with the exception of bio-based diesel synthesized using the Fischer-Tropsch method (Gupta & Demirbas, 2010).

Free Fatty Acids. Cleavage of the fatty acid from the glycerol molecule is most commonly achieved via hydrolysis during oil processing and extraction. This produces free fatty acids (FFA). This also explains in part the increased presence of free fatty acids in fryer oil the longer it is used. The presence of water and FFAs reduce yields by consuming catalyst and feedstock in the production of unwanted soaps (Kusdiana & Saka, 2004). For the purpose of transesterification, increased FFA content reduces the potential yield of biodiesel because the FFAs are neutralized and drop out in the glycerol. The excess of FFA where acid-catalyzed esterification is concerned actually improves reaction time. However, esterification is much slower compared to base-catalyzed transesterification (Kusdiana & Saka, 2004).

Alcohol. The process of making biodiesel requires the use of an alcohol which is attached to the fatty acid by a catalyst. This produces an ester, which is then labeled according to the alcohol that has been used. Thus, we commonly see the names fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE) attached to biodiesel based on the alcohol used.

Catalyst. Catalysts used to produce biodiesel can be acidic, basic, or enzymatic. The most common base catalysts are potassium hydroxide (KOH) or Sodium hydroxide (NaOH). Common acids include sulfuric, hydrochloric, and sulfonic acids (Gupta & Demirbas, 2010).

General Reactions

There are four basic reactions that must be considered during the production of biodiesel, summarized in equation form below (Guibet, 1999). Different reaction paths can be taken to arrive at an end-stage ester or biodiesel; however, these reactions provide the general overview of hydrolysis, saponificaiton, esterification, and transesterification:

Hydrolysis: Triglyceride + Water $\leftrightarrow$ Free Fatty Acids + Glycerol

Esterification: Free Fatty Acid + Alcohol $\leftrightarrow$ Ester + Water

Saponification: Triglyceride + Base $\leftrightarrow$ Metallic Salt (soap) + Glycerol

Transesterification: Triglyceride + Alcohol $\leftrightarrow$ Ester + Glycerol

Biodiesel can be produced using acidic, basic, or enzymatic catalysts and supercritical reactions in various combinations (Basah, Gopal, & Jebaraj, 2009). The most common method of biodiesel production, however, remains that of base-catalyzed transesterification (Gupta & Demirbas, 2010). This process occurs in three consecutive and reversible step-wise reactions as illustrated by the reaction equations below. A catalyst is attached to an alcohol (R+OH) and then collides with a triglyceride. A triglyceride is converted to diglyceride, then to a monogylceride, and finally a glycerol (Gupta & Demirbas, 2010).

$$\text{Triglyceride} + \text{ROH} \leftrightarrow \text{RCOOR}_1 + \text{Diglyceride}$$

$$\text{Diglyceride} + \text{ROH} \leftrightarrow \text{RCOOR}_2 + \text{Monoglyceride}$$

$$\text{Monoglyceride} + \text{ROH} \leftrightarrow \text{RCOOR}_3 + \text{Glycerol}$$

Molar Ratios

Transesterification can be understood best in terms of molar ratio. During transesterification, each triglyceride is broken down into three esters and a glycerol molecule. This means that for each mole of oil three moles of alcohol are required, so at the completion of the reaction the molar ratio is 3:1. The kinetics of transesterification requires a surplus of alcohol and experience has shown that a 6:1 ratio of alcohol to oil is required. The catalyst is frequently conveyed in terms of weight in relation to the alcohol. NaOH, for instance, is expressed as 5% by weight of the methanol. This is a 25:1 molar ratio of alcohol to catalyst. Catalyst and alcohol values can be flexible, but changes in these molar ratios can present problems. If there is not enough alcohol easily available for the catalyst it will begin to react with triglycerides and create soap, which is why there must be enough alcohol available after the transesterification process to chemically occupy the catalyst as well as to drive the reaction. Insufficient catalyst results in more time in order to complete a reaction.

ASTM Fuel Specifications

Fuel Characteristics and ASTM Specifications

The American Society for Testing and Materials (ASTM) specifies standards for biodiesel in the United States. In the US, the battery of tests that pure biodiesel must pass are grouped and referred to as ASTM D6751-09 (See Table 2.7) (ASTM International, 2009a). Stock used specifically for B6-B20 blends (those fuels that are a mix of petro and biodiesel) can be tested under slightly different specifications (ASTM International, 2009b). All ASTM specifications require biodiesel to meet the same standards irrespective of feedstock. Feedstock and transesterification processes do have an effect on fuel characteristics (Demirbas A. , 2007).

Biodiesel Use and Emissions

Advantages and Disadvantages

Biodiesel is a renewable and non-petroleum based liquid fuel that can substitute for the use of petroleum diesel. Minor, if any, modifications are required for use of biodiesel in current diesel engines for operation. These modifications are generally issues pertaining to fuel system materials compatibility (Kemp, 2006). Biodiesel is less toxic and biodegradable, reducing pre-combustion emissions associated with fuels (Guibet, 1999). Post-combustion emissions such as particulate matter (PM), carbon monoxide and dioxide (CO/CO_2), non-methane hydrocarbon (HC), and other non-regulated emissions are generally reduced. Nitric oxide(NO) and nitrogen dioxide (NO_2), however, are not always reduced and continue to be a focus of emissions reduction efforts as they pertain to biodiesel (Sun, Caton, & Jacobs, 2010). Both oxides of nitrogen are jointly termed “NOX” but written as NO_x. The issue of

NO_x, as well as a lower heating value, reduced cold flow properties, lower volatility, higher viscosity, and a shorter shelf life all remain obstacles to biodiesel adoption (Gupta & Demirbas, 2010; Worldwatch Institute, 2007).

Table 2.7
Summary of ASTM Tests Required for Biodiesel and Blend Certification

Property	Method	Limits		Units
Calcium & Magnesium, combined	EN 14538	5	max.	ppm (ug/g)
Flash Point (*closed cup*)	**D 93**	**93**	**min.**	**C°**
Alcohol Control (*One of the following must be met*)				
1. Methanol Content	EN14110	0.2	max.	% mass
2. Flash Point	D93	130	min.	°C
Water & Sediment	**D 2709**	**0.05**	**max.**	**% vol.**
Kinematic Viscosity, 40 C	**D 445**	**1.9 - 6.0**		**mm2/sec.**
Sulfated Ash	D 874	0.02	max.	% mass
Sulfur				
S 15 Grade	**D 5453**	**.0015 (15)**	**max.**	**% mass (ppm**
S 500 Grade	**D 5453**	**.05 (500)**	**max.**	**% mass (ppm**
Copper Strip Corrosion	**D 130**	**No. 3**	**max.**	
Cetane	**D 613**	**47**	**min.**	
Cloud Point	**D 2500**		**report**	**C°**
Carbon Residue 100% sample	D 4530*	0.05	max.	% mass
Acid Number	**D 664**	**0.5**	**max**	**mg KOH/g**
Free Glycerin	D 6584	0.02	max.	% mass
Total Glycerin	D 6584	0.24	max.	% mass
Phosphorus Content	D 4951	0.001	max.	% mass
Distillation, T90 AET	**D 1160**	**360**	**max.**	**°C**
Sodium/Potassium, combined	EN 14538	5	max.	ppm
Oxidation Stability	**EN 14112**	**3**	**min.**	**hours**
Cold Soak Filtration	Annex to D6751	360	max.	seconds
For use in temperatures below -12 C	Annex to D6751	200	max.	seconds
Unique to Biodiesel Blends B6-B20				
Ash Content	**D 482**	**0.01**	**max.**	**% mass**
Carbon Residue 10% sample	**D 524***	**0.35**	**max.**	**% mass**
Lubricity, HFRR at 60C	**D 6079**	**520**	**max.**	**microns**
Biodiesel Content, % (V/V)	**D 7371**	**6.-20.**	**range**	**% Vol.**

Note: Bold text indicates test performed on blends. All Blending Stock must pass ASTM B100 Tests before blending

Emissions and Regulation

Combustion of fuels within the transportation sector represents a large fraction of overall energy use and emissions (Kaiper, 2004). Regulative action in Europe and the United States came into effect during the 1960s and 1970s (Guibet, 1999). The goal of regulation has, in part, been to reduce emissions that are harmful to the environment. Carbon dioxide and methane are greenhouse gases (GHG), yet regulation for these two gases is not yet directly addressed in industry or vehicle emissions in North America (Kemp, 2006). Regulations do limit the amount of carbon monoxide (CO), nitrogen oxides ($NO_{x)}$, sulfur oxides (SO_x), non-methane volatile hydrocarbons (HC), and particulate matter (PM). These emissions are considered to have a greater detrimental effect on the environment. Comparison of these compounds to CO_2 and their global warming potential (GWP) has been the subject of extensive study to define compounds in terms of carbon dioxide equivalent (CO_2e) (Forster et al., 2007)

Emissions Mitigation Strategies

Several methods have been developed to mitigate vehicle emissions. Catalytic converters have been placed in exhaust lines to complete partial combustion reactions. Fuel characteristics and composition have also been changed, in particular the reduction of sulfur in diesel, to promote more complete combustion and to reduce emissions of regulated compounds such as CO, NO_x, and SO_x. Engines and control systems have been designed to better control the timing of fuel injection for improved engine performance and to achieve a general reduction in emissions generation (Guibet, 1999).

Biodiesel Versus Petroleum Emissions

When biodiesel and petroleum diesel are compared holistically, total GHG emissions are significantly reduced and offset (Sheehan, Camobreco, Duffield, Graboski, & Shapouri, 1998). A holistic comparison is dependent on total petroleum-based emissions generated during production, emissions from vehicles, and total CO_2 offset by crop sequestration.

Because the two fuels differ in characteristics, method of production, and emissions, it is important to note how biodiesel is compared to petro-diesel. The United State Environmental Protection Agency (EPA) showed that pure biodiesel used in conventional heavy-duty diesel engines increased NO_x emissions by 10% compared to conventional diesel. In contrast, CO and PM were reduced by approximately 48%. HC saw the greatest reduction at approximately 78% . Emissions varied depending on the type of biodiesel feedstock as well as the type of conventional diesel with which it was blended (US Environmental Protection Agency [EPA], 2002). Further research has shown that NO_x emissions are not consistently higher across fuel blends, particularly when accounting for new engine design. Differences do occur across engine type, technology, and operating conditions, as well across feedstocks (Sun et al., 2010). NO_x remains the primary obstacle for biodiesel in terms of emissions and is a focus of the emissions data for this study.

Testing and Quantifying Post-Combustion Emissions

Post-combustion emissions regulations are quantified in terms of mass per distance accumulated for light-duty vehicles and mass per unit of energy produced for commercial vehicles. Emissions samples are collected from the exhaust line by a constant volume sampler (CVS) measuring system. Heated filters, chillers, flame ionization detectors (FID), non-dispersive ultraviolet (NDUV) analyzer, and non-dispersive infrared (NDIR) analyzers are used to test particulates and gases during standardized operating conditions. Light-duty vehicles are typically tested on dynamometers and run through standard driving cycles. Heavy-duty engines are typically installed on a test bench and emissions recorded for speed and load separately (Guibet, 1999). The controlled tests established for regulation purposes do not necessarily mimic on-road driving conditions, however.

Chemical Formation of Nitrogen Oxides

Oxides of nitrogen are the primary pollutant expected to increase during the use of biodiesel. Understanding the formation of the gas and potential mitigations of the gas has been the focus of substantial research (Sun et al., 2010). The formation of NO or NO_2 is described by the three reversible equations in shown below (Bowman, 1975). The formation of nitrogen oxides increases exponentially with the increase of combustion temperatures (Dean & Bozzelli, 2000). Fuel-bound nitrogen is considered to be less important to the formation of oxides of nitrogen than is the thermal mechanism (Sun et al., 2010).

Equation 1: $O + N_2 \leftrightarrow NO + N$

Equation 2: $N + O2 \leftrightarrow NO + O$

Equation 3: $N + OH \leftrightarrow NO + H$

Fuel Properties

Physical and chemical. Fuel is tested for physical and chemical properties. Physical properties mainly affect physical processes such as density, while chemical properties mainly affect chemical processes such as energy conversion. Biodiesel fuel and blends are regulated by established ASTM standards (see Table 2.7) for general inclusion into the petro-diesel infrastructure. Physical properties such as viscosity and density affect injection timing and fuel atomization and can indirectly affect combustion and emissions formation by varying engine system responses (Sun et al., 2010) See table2.8. Chemical properties such as hydrocarbon structure and aromatic content tend to dominate a fuel's effect on combustion and emissions formation (Sun et al., 2010).

Fuel Characteristics and Engine Response

The diesel engine industry has designed engines for petroleum-based fuel. Although diesel engines can run on biodiesel, the combustion and emissions profiles are different. The fuel to be used in an engine remains a primary design parameter. Furthermore, extensive research has led to the conclusion that certain increases in pollutants such as NO_x cannot be mitigated or controlled simply by changing a fuel property, but rather are "the result of a number of coupled mechanisms whose effects may tend to reinforce or cancel one another under different conditions, depending on specific combustion and fuel characteristics"(p.1) (Mueller, Boehman, & Martin, 2009,p. 1). Potential contributions to differences in NO_x emissions can relate to injection in terms of timing, delay, pressure, spray characteristics, and mixing. Combustion stages, heat release, radiation from soot, and temperatures are also suspected to increase emissions (Sun, Caton, & Jacobs, 2010)

Major differences in fuels require adjusting the underlying engine technology (Jeschke, 2009). Adjustments in heat management, fuel conditioning, fuel forwarding, and injection can improve overall efficiency and emissions. The primary difference between biodiesel and petroleum-based fuels is the oxygen content (Demirbas, 2009). The chemical properties are different and, consequently, the nature of combustion is also different (Guibet, 1999). The presence of oxygen in the biodiesel molecules reduces the fuel's compressibility (high bulk modulus) compared to petro-diesel, which is comprised primarily of hydrocarbons (Szybist, Kirby, & Boeham, 2005). Fuel viscosity, which is affected by compressibility, can artificially advance fuel injection timing (Sun et al., 2010). This may occur by minimizing system designed leakage due to higher fuel viscosity increasing fuel system pressure and consequently advancing injection timing. Advanced injection timing changes time of combustion and combustion temperatures and can result in NO_x formation. This passive system response can affect controlled system responses from the engine as it attempts to change injection parameters in order to control noise, efficiency, and emissions. Diesel engines vary in design, and consequently passive and controlled responses vary affecting emissions as shown in Table 2.8 (Sun et al., 2010).

Table 2.8

The Effects Of Property Difference Between Biodiesel or Its Blend and Petroleum Diesel On Engine Parameters.

	Difference	Injection timing	Injection pressure	Fuel spray penetration	Fuel spray angle	Fuel spray atomization	Ignition delay	Heat release	Combustion temperature
Physical Properties									
Liquid density[a]	+	+	+	-	-		+		
Bulk modulus of compressibility[b]	+	+	+	+					
Speed of sound[b]	+	+	+	+					
Liquid viscosity[a]	+	+			-	-	+		
Surface tension[a]	+	+		+		-			
Vapor pressure[a]	-	-				-	+		
Volatility[c]	-					-			
Liquid specific heat[a]	-					+	-		
Vapor specific heat[a]	-					+	-		
Heat of vaporization[a]	+						-		
Chemical Properties									
Chain length[d]	+	-					-		
Oxygen content[c]	+	+						+	+
Aromatics content[e]	-	+						+	+
Sulfur content[f]	-							+	
Saturation (iodine value)[d]	-						+		+
Cetane number[g]	+						-		
Heating value[c]	-								-

NOTE: A plus sign in the "difference" column indicates biodiesel has a higher value of the listed property relative to petroleum diesel. A plus sign in the remaining data columns indicates the corresponding difference in the property increase or advances the respective engine parameters. A minus sign indicates a decrease or a retarding.

NOTE: Table from "Oxides of nitrogen emissions from biodiesel-fuelled diesel engines: by J. Sun, J. A. Caton and T. J. Jacobs, *Progress in Energy and Combustion Science,36,* 677-695

CHAPTER 3

RESEARCH METHODOLOGY

Introduction

The research methodology has been organized into five primary sections. These include a brief contextual overview of the trip to the Democratic Republic of Congo (DRC) in January, 2010, and a rationale for the variety of pulp processing methodologies used. The methodologies are organized chronologically to make clear the progression from feedstock collection to final fuel testing. The sections are organized in the following order: Field Data, Fruit Pulp Processing, Oil Pressing and Refining, Biodiesel Production and Polishing, Biodiesel Characterization Tests, and finally, Emission Tests. Although the last two sections detail the primary focus of this research, the chronological progression of sections should help readers better understand the research methodology and the relevance of the results.

Contextual Overview

Traveling to the DRC

Because Safou oil is not a readily traded commodity in the countries in which the fruit grows, acquiring oil for testing was complicated. In May 2009, I was able to get initial samples of fruit pulp from the DRC to conduct preliminary tests regarding fruit pulp processing for oil, fuel production, and a preliminary fuel characterization. Further research required a larger oil sample as well as field data and process data, which required traveling to the DRC. This occurred during a two-week period from January 7 – January 21, 2010, made possible via a travel grant from Appalachian State University's Office of Student Research.

During the short time field data was collected, approximately 250 kg of fruit was processed for export.

My initial goal was to return with only oil, but that was not possible due to several complications. First, fruit was not readily available in the Kinshasa area because the fruiting season was delayed. This meant fruit was sparse in the local markets and acquiring fruit required more time than allotted. Secondly, even though the manual PITEBA screw press did work, it required more time than was available to process all the fruit for the planned departure. Thirdly, processing the fruit, which included splitting the fruit in two, scooping out the central seed cluster, then chopping the fruit up before drying, was time consuming. These factors led to a focus on drying pulp for transport to the United States where it would then be run though a screw-press. All fruit samples had to be processed according to guidelines established by the United States Department of Agriculture so that it could pass the Customs inspection process on entry to the US. The approved methodologies for processing included drying and canning the fruit.

Standardizing the fruit pulp process would have been ideal; however, time constraints forced the use of all available means of preparing pulp for export. This did introduce variables regarding processing, but the methods used were not expected to affect fatty acids at the molecular level. Consequently, the biodiesel derived from the oil, regardless of processing method used, was still considered representative of the fruit's potential as a fuel source.

The majority of the fruit pulp was either dried using forced air electric dehydrators or roasted using standard convection ovens. A smaller sample of wet pulp (14 jars) was pressure canned for later drying. The dried fruit, weighing approximately 65 kg, was vacuum-packed in Ziploc bags and heat-sealed and labeled. Samples were packed in a trunk for shipment to the United States accompanied by a letter explaining the research and the sample's adherence to USA regulations pertaining to the import of agricultural material. Once in the United States the dried fruit pulp was run through a screw press to harvest the oil.

Data regarding oil yields and raw oil characteristics were collected prior to refining for biodiesel conversion. Several preliminary conversion methods were used to identify a maximum biodiesel yield and included single-stage base-catalyzed transesterification reactions, a single-stage acid-catalyzed esterification reaction, as well as a two-stage acid then base catalyzed reaction. The two-stage acid then base-catalyzed reaction was used for the test fuel.

The test fuel was polished in order to produce fuel that would potentially pass ASTM criteria prior to emissions testing. This polished fuel was then used for fuel characterization and emissions tests. Emission testing was performed under monitored outdoor conditions on an on-road test course.

Field Data

Harvesting Data

Seven trees were harvested; however, tree morphology varied considerably as did the fruits' readiness to be harvested. Methods of harvesting were observed and documented, as were the number of people involved, the time required, and the amount of fruit harvested.

Market Data

This data included price for fruit, quantity collected, and the state and quality of the fruit. Fruit price varied but is representative of the low supply/high demand period of the Safou season. The state of the fruit that is considered marketable as well as various morphologies in the fruit sold was noted.

Fruit Pulp Processing

Fruit Samples

Criteria for inclusion. Fruit samples were included if they had achieved a level of maturity deemed by local markets as edible. Three general types or morphologies of fruit were collected, but in all cases ripeness was determined by the predominance of dark bluish purple coloring on the fruit skin. While a large portion of the fruit harvested was characterized as near ripe with residual pinkish spots on the skin, the majority of the fruit was fully ripe. Furthermore, over 70% of the sample fruit was purchased at local markets, ensuring a sample representative of marketable fruit from local industry.

Criteria for spoiled fruit. Safou fruit is firm when ripe and softens rapidly as it spoils. Any fruit that was soft and easily deformed was included in the spoiled sample. Such fruits were culled each day from the unspoiled fruit and processed separately.

Decorticating the Fruit

Ripe and near-ripe fruit. Ripe and near-ripe fruit is firm. The fruit was split in two halves using a knife. The seed cluster was then removed with a spoon. This left the fruit skin and the membrane of the seed cluster still attached to the pulp. This pulp then underwent drying or roasting.

Spoiled fruit. Spoiled fruit pulp is soft and mushy and separates easily from the seed cluster. This separating was done manually. These pulp samples did not include the outer membrane of the seed cluster and had less of the fruit's outer skin. This pulp then underwent drying, roasting, or canning.

Fruit Drying

Fresh and spoiled pulp that had been removed from fruit was placed in various forced air food dehydrators for 6-12 hours until the fruit pulp had lost a minimum of 60% of its original weight. The pulp was dried until it would snap when attempting to bend it. The fruit was weighed prior to the drying process and then at various intervals thereafter until the total weight was less than 40% of the original minus the drying trays. Three food dehydrators were used including a 300-watt updraft Oster, a 300-watt updraft Magic Chef, and a 500-watt downdraft NESCO. The stackable trays were rotated bottom to top whenever the trays were being individually weighed.

Oven drying.

Non-canned pulp. The oven drying used on fresh and spoiled pulp was more akin to roasting and was only used on the pulp that had not been canned. Fruit pulp was weighed prior to being placed in the oven and then was removed when it had been reduced to less than 40% of its original weight. Fruit pulp was placed in various ovens set at 250° F to 300° F. These temperatures were chosen to accelerate drying times while remaining well under the 375° F threshold when triglycerides begin to volatize. The oven door was propped open about a half inch with the use of wooden spoons. The pulp was stirred every half hour and rotated from top to bottom if several trays were in the oven at one time. Total time in the oven was usually about 2.5 - 3 hours. Pulp was considered ready for removal and cooling when shaking the tray back and forth revealed no pulp sticking to the tray and produced a dry brittle sound. Both fresh fruit and spoiled fruit were dried for export in this manner.

Canned pulp. Canned pulp was oven dried once it arrived in the United States. Because there was no time constraint, oven temperature was set to 210° F. The tray was weighed and recorded every half hour. At the point when there was less than a gram of weight change over the course of an hour the pulp was removed from the oven, allowed to cool, and placed in a plastic bag for storage.

Canning

All pressure canning was done with glass jars with sealable lids. The jars were canned at 15 psi, raising the temperature to approximately 250° F. Once the pressure cooker was at pressure it was kept on heat for 30 minutes, after which the pressure cooker was rapidly cooled with water until pressure equalized with ambient pressure. Jars were labeled and packed for export. Once the cans were imported to the United States samples were removed from the jars and oven dried.

Before initial placement in the canning jars, fruit processed via this preparation method were subject to one of four pretreatments. The methods described here were done to identify feasibility and simply to get as much undried fruit pulp ready for export to the United States.

Pretreatment one.

Whole fruit: fresh. Approximately 400 ml of whole fruits were placed in canning jars with 200 ml of water. Samples were then canned.

Pretreatment two.

Whole fruit: wilted. Whole fruits were placed in an oven at 200° F for approximately 45 minutes to wilt. These whole fruits were then placed in canning jars with no water. Samples were then canned.

Pretreatment three.

Fruit pulp: blanched. Whole fruits where blanched in boiling water for 5 minutes. The pulp was then scraped from the seed cluster by hand and packed in canning jars. Samples were then canned.

Pretreatment four.

Fruit pulp: spoiled. Spoiled fruit pulp was scraped from the seed cluster and packed in jars. Samples were then canned.

Establishing Zero Moisture Content

In order to establish a zero moisture content, samples that had been dried in the food dehydrators in the DRC where then placed in a muffle furnace for a minimum of 24 hours at 212° F (100°C).

Safou Pressing and Oil Refining

Pre-press Pulp Conditioning

Dried fruit pulp was crumbled using a Kitchenaid® flourmill. The grinder was set with a ¼ inch gap to crumble the dried pulp. This pretreatment was done to help the flow of dried fruit through the hopper and into the press. If pulp was not dry enough to crumble in the mill it was not dry enough to progress through the press.

Oil Pressing

The press. Pressing was done using a Taby 20 bench-top extrusion screw-press made in Sweden. The Taby model expresses oil at its mid-point and extrudes meal pellets at the end opposite the hopper. This press has a heating collar that goes around the press housing where the extrusion dyes are inserted.

Preparing the press. The press was cleaned using mild soap and water and was allowed to thoroughly dry before pressing. Once assembled, the press was allowed to heat thoroughly with the heating collar before pulp was introduced into the press.

Heat and moisture control. The heating collar was regulated by a thermostat attached to the housing to maintain temperatures between 100-150° C. When pulp was excessively dry and threatened to bind up the press, moisture was introduced to the feedstock. The moisture was added by misting the feedstock while in a stainless steel Kitchen Aid mixing bowl. The feedstock was thoroughly mixed and tumbled before being placed in the hopper.

Labeling

Labeling on samples included the original quantity of fresh pulp, how it was processed, as well as its final dry weight. Glass vessels in which the oil was collected were labeled with the vessel's dry weight (including the label), how it was previously processed, as well as its final oil sample weight. Press-meal was returned to the original container in which the pulp had been processed and the final press-meal weight recorded.

Oil and Press-meal Capture

The oil was captured in glass vessels. These vessels were thoroughly cleaned with soap and water and then rinsed with pure acetone. The press-meal was collected into a glass bowl and then transferred to the jar or bag in which it had been imported.

Oil Yield Calculations

Oil yield was determined by weight. Complete calculations required corrections for pressing losses, moisture content, and foots (sediment).

Press losses. In the course of pressing a feedstock, a certain quantity of the feedstock does not progress through the press, as well as oil that remains on the press. Material loss was calculated by subtracting the dirty press weight from the clean pre-pressing press weight. Unaccounted for weight was considered to be moisture losses due to evaporation.

Single sample. All parts for the press assembly were cleaned and weighed to establish a pre-press weight. Sample material that failed to progress through the press was determined by placing the entire press housing on a scale and subtracting the pre-pressing weight from the post-press weight. The weight of material that did not make it through the press was excluded from the yield calculations.

Multiple sample runs. When multiple samples were run in sequence, a starter sample was used to fill the press housing and excluded from any yield data. Subsequent samples were introduced once the press had run for two minutes, beginning when meal ceased to progress through the extrusion dyes. Oil vessels were changed and the press meal stored in its original container.

Moisture content. During the course of pressing moisture content is lost due to evaporation and must be accounted for in yield calculations. The sum of the raw oil expressed and the press-cake will not equal the original feedstock sample weight. Some moisture is contained in the oil while the majority remains in the press-cake and then evaporates. Moisture content is best determined before expression by desiccating a sample of the feedstock. This percentage can then be applied to the equation, or the percent yield can be qualified with percent moisture of the starting feedstock. This strategy was used in this study.

Foots/Settling. Non-oil material was accounted for using a 100 ml graduated cylinder. The raw oil vessels were place in an oven at 175º F for one hour. The oil catchment vessel was then shaken for 1 minute in order to re-suspend sediment. This suspension was then poured into a graduated cylinder. The graduated cylinder was then placed in the oven again for a minimum of four hours at 175º F, at which point the oven was turned off and the cylinders allowed to settle for a total of 24 hours. The volume of the sediment was then subtracted from the original volume.

Oil Purifying

After being captured in the glass vessels, the oil was placed in the oven for a minimum of four hours at 175° F. This helped to settle particulate matter (foots) and further dry the oil. After the oil had been settled the oil was poured out into secondary vessels, taking care to avoid the transfer of foots.

Several methods of filtering the oil were used. The oil was first filtered through a metal coffee filter, but this still allowed small particulates through. Coffee filter paper was then used, which did an excellent job of purifying the oil but was slow. The process was also only possible when the oil was warm, which required it to be heated in an oven at 175° F.

A centrifuge proved to be the most effective method for removing particulates. The oil was heated to 175° F before being run through the centrifuge. The centrifuge was a bowl design unit built by Simple Centrifuge and constructed of 6061-T6 aluminum for chemical resistance. Large light material that made it through the centrifuge was then removed using a bucket filter. Centrifuge oil was stored in a five-gallon bucket made of high-density polyethylene (HDPE). The final oil sample produced for biodiesel production was approximately four gallons.

Biodiesel Reactions and Fuel Polishing

Titration

Oil was titrated to determine how much free fatty acids were in the feedstock and how much catalyst would be needed for base-catalyzed reactions in order to complete the biodiesel reactions. The titer used was a solution prepared by placing a gram of catalyst in a one liter volumetric flask to the one liter mark with distilled (de-ionized) water. The titration procedure required the sample, the titer solution, 91% pure isopropyl alcohol, and phenolphthalein as an indicator. Twenty-five milliliters of isopropyl alcohol was placed in a 150 ml beaker along with one milliliter of sample and three drops of phenolphthalein. The solution was agitated while the titer was slowly introduced until a pink color change was observed and maintained for 30 seconds. The number of milliliters of titer required for the color change is indicative of the grams of catalyst required to neutralize a liter of feedstock. This procedure was repeated at least three times and the values averaged to arrive at the amount of base catalyst required to neutralize the free fatty acids.

Biodiesel Reactions

Several reactions were bench top tested for the production of biodiesel. These included two NaOH base-catalyzed reactions as well as a two-stage acid then base reaction. The reactions are summarized below. The oil feedstock, and not necessarily the transesterification process, affects the fuel composition. Reaction methods are in general chosen primarily in terms of yield, consumables, process energy balance, and time.

After several bench top tests, the two-stage test was chosen for fuel production because optimal yield appeared to be around 85% to 90%, indicating a near complete reaction. However, up-scaling the smaller bench top reaction proved to be less successful when the final 12.33 liters of oil were reacted.

Reaction one: NaOH base.

Reactants. These tests were done with 10 grams of raw centrifuged Safou oil. Transesterification was done using NaOH and methanol. The molar ratio of methanol to oil was 6:1. NaOH catalyst was 5% by weight of methanol.

Reaction vessel. Ingredients were placed in a three-necked round bottom flask. A glass stirring apparatus was placed in the central neck. A cork was placed on another neck while the last neck received a distillation column, virtually closing the system.

Time and temperature. The batch was heated to 50° C for one hour.

Washing. The reaction solution was rinsed out of the reaction vessel into a 125 ml separatory funnel using 30 ml of ethyl acetate, and then poured into a 125 ml separatory funnel. 30 ml of de-ionized water was placed in the separatory funnel with the reaction solution and agitated three times, relieving any pressure build-up between agitations. The water and biodiesel were then allowed to separate out for a minimum of 10 minutes. The water was then drained. The wash procedure was repeated three times.

Post-wash purifying. Washed biodiesel/ethyl acetate solution was dried with the addition of magnesium sulfate ($MgSO_4$). The dried solution was then filtered through filter paper to remove the magnesium sulfate. The final step was to evaporate the ethyl acetate using a rotating evaporator. Biodiesel was then placed in a glass vial for storage.

Reaction two: NaOH base.

Reactants. These tests were done with 150 ml of gravity-settled Safou oil. The transesterification was done with 5.5 ml of sodium methylate and 37.5 ml of methanol. This is equivalent to a 6:1 molar ratio of methanol to oil and NaOH catalyst of 5% by weight of methanol.

Reaction vessel. Ingredients were placed in a 500 ml Erlenmeyer flask and placed on a hot plate with a magnetic stir bar. A plastic funnel was placed in the neck of the Erlenmeyer flask to reduce methanol escape. A glass thermometer was inserted to monitor temperature.

Time and temperature. The batch was heated to 50° C for one hour and the glycerin was allowed to settle out for 8 hours.

Washing. After settling, the biodiesel fraction was decanted out into a 500 ml separatory funnel. 400 ml of tap water was placed in the separatory funnel with the reaction solution and agitated three times, relieving any pressure build-up between agitations. The water and biodiesel were then allowed to separate out for a minimum of 10 minutes. The water was then drained. The wash procedure was repeated until rinse water was mostly clear with only slight haze.

Post-wash purifying. Washed biodiesel was then de-methylated and dried by placing it in a 250ml beaker and raising the temperature to 100°C for 10 minutes while being stirred.

Reaction three: two-stage acid-base reaction. Reaction three was a two-stage reaction. The first stage, an acid-catalyzed esterification reaction, was followed by a second stage base-catalyzed transesterification reaction.

Stage 1: reactants. 150 ml of centrifuged and filtered oil was mixed with 8% by volume of methanol. Sulfuric acid (98% pure H_2SO_4) was added at a ratio of 1ml per liter of oil.

Stage 1: reaction vessel. The reactants were placed in a 500 ml Erlenmeyer flask. A funnel was placed in the neck of the flask to reduce any methanol escape and a thermometer was inserted to monitor temperature. The flask was then placed on a hot plate with magnetic stir bar.

Stage 1: time and temperature. The solution was then held at 36° C for one hour while being stirred. The solution was then stirred for another hour and the temperature allowed to decrease to room temperature. The acid reacted vessel was then allowed to settle for 8 hours.

Stage 2: reactants. Methanol and 30% concentrate sodium methylate were added to the reaction vessel. The total methanol in the reaction, including the fraction in the sodium methylate, totaled 14%. The total percentage by volume of stage-one and stage-two methanol then totaled 22%.

Stage 2: reaction vessel. The reaction vessel remained the same as in stage one.

Stage 2: time and temperature. The solution was then reacted for 1 hour at 50° F while being constantly stirred. It was then allowed to settle for eight hours.

Washing. After settling, the biodiesel fraction was decanted into a 500 ml separatory funnel. 400 ml of tap water was place in the separatory funnel with the reaction solution and agitated three times, relieving any pressure build-up between agitations. The water and biodiesel were then allowed to separate out for a minimum of 10 minutes. The water was then drained. The wash procedure was repeated until rinse water was mostly clear with only slight haze.

Drying and de-methylating. The fuel was stirred while the temperature was raised to 60º C and maintained for 10 minutes after boiling ceased.

Test fuel reaction methodology. Test fuel was produced following the third reaction, using the two-stage reaction. The raw Safou oil was titrated and determined to have a considerably high free fatty acid (FFA) concentration. Rather than neutralize the FFAs and lose them in the glycerin the fuel yield was increased by doing a two-stage reaction including acid-catalyzed esterification followed by base-catalyzed transesterification.

Stage 1: reactants. 986 ml methanol (8% by volume) was added to 12.33 L of raw centrifuged and filtered Safou oil. While the methanol and oil were being stirred, 12 ml of sulfuric acid (98% pure H_2SO_4) was added.

Stage 1: reaction vessel. The reactants were placed in a five-gallon bucket made of HDPE. A mixing rod was threaded through the bucket lid to a corded drill. The drill was fixed in place by a vise and a variable voltage dial was used to control the speed of the drill for mixing.

Stage 1: time and temperature. The reactants were mixed for 1 hour while being held at 36° C using a thermometer and bucket heater. After the first hour the bucket heater was removed and the reactants mixed for an additional hour. The solution was allowed to settle for more than eight hours.

Stage 2: reactants. 2.08 L of methanol was then mixed with 0.483 ml of sodium methylate in a five-gallon bucket. This mixture was then added to the stage one reactants, but only after they were moved to a different reaction vessel. After the addition of the stage two reactants, a quantity of solution was drained into the bucket that had the stage two reactants to rinse and pour back in the stage two reactor.

Stage 2: reaction vessel. The reactants from the stage one reaction were placed in a 50 gallon HPDE graduated reaction vessel. The vessel was raised up so that a five-gallon bucket could easily be placed under it. The corded drill and variable speed apparatus were installed as well as the bucket heater and thermometer.

Stage 2: time and temperature. The temperature in the reaction vessel was raised to 55° C and contents were mixed for two hours. The reactants were then allowed to settle for over 24 hours.

Washing. After draining the glycerin fraction the fuel was then washed with a fine mister and the water drained. Fifteen gallons of water were used for the washing process.

De-methylating and drying. Once the water was drained the bucket heater was used to raise the fuel temperature to 60° C for 10 minutes to de-methylate the fuel. The fuel was then allowed to settle for 24 hours in order to allow available water to precipitate out.

Fuel polishing.

Purolite. The mostly dry and de-methylated fuel was then run four times through a column of Purolite ion exchange resin. Water content was still at 2400 ppm when the maximum water content can be 2400 ppm.

Magnesol. After several tests showed that the fuel was still not ASTM certifiable after the Purolite treatment, a 3% by weight quantity of Magnesol (magnesium silicate) was added to the biodiesel. The fuel and Magnasol was agitated for 10 minutes and then allowed to settle for at least 24 hours before being filtered.

Filtering. After settling, fuel was vacuum filtered. A filter with a rubber gasket was placed in the throat of an Erlenmeyer flask, which also had a nipple on the collar to pull a vacuum. Line was then run from the Erlenmeyer flask to a ten-gallon carboy through a double-holed cork. Another line then exited the carboy via the second hole in the cork and went to the dry vacuum pump. A Number 1 qualitative filter paper was used in the filtering funnel. Once fuel was placed in the filter funnel a vacuum of -15psi was maintained during filtering. The filtered fuel was collected in the 500 ml Erlenmeyer flask. When the flask was full, the vacuum was released and the funnel removed in order to empty the filter fuel into the final storage container.

Test Fuel Storage. After filtration, fuel was stored in a standard red two-gallon plastic gas can.

Oil And Fuel Characterization

Energy Content

Calorimetry tests were conducted using a Parr oxygen bomb calorimeter. Temperature change data was collected using native software. Standard procedures outlined in the Parr instruction manual were followed. The heat of combustion was calculated from the change in the water temperature; however, the rise in temperature had to be corrected for wire combustion and acid production. The energy released in the bomb by the element that lights the reaction was subtracted from the change in temperature recorded. Furthermore, the production of sulfuric acid during combustion was actually endothermic so the energy consumed from this reaction had to be back-calculated. This calculation was derived by collecting the condensation on the inside of the oxygen bomb, which was saturated with acid. To determine this, a small piece of pH paper was used. If the paper indicated the presence of acid it was necessary to determine the quantity of acid and what kind of acid was present. The acidic condensate was rinsed out of the oxygen bomb with a small amount of de-ionized water. The acidic rinse water was then titrated, followed by a series of chemical reactions that precipitated out specific acid fractions to determine how much of an acid was generated during combustion of the bomb. The procedure followed is one outlined in the Parr Oxygen Bomb instruction manual.

Fuel Characterization Tests

Hydrogen nuclear mass resonance. Oil and fuel composition was determined using HNMR. Samples were placed in HNMR test tubes and suspended in deuterium chloroform ($CDCl_3$). This test exposes molecules to a magnetic field and bombards the sample with electromagnetic pulses. Based on the mass and hydrogen placement in the molecules, the compounds resonate at the atomic level, emitting energy at certain frequencies. The molecular structure can be determined based on the points of resonance.

Gas chromatography / mass spectrometry (GC/MS). Fuel samples were placed in the GC/MS device. This test was able to identify the primary chemical compounds in the fuel with a high degree of accuracy. The methodology for the biodiesel test conducted requires the vaporization of the fuel at 250° C prior to its entrance into the column. For the methodology used the column began at 160°C and the temperature was increased at a rate of 8° C per minute until a maximum temperature of 250° C was reached and held for 1 minute. The sample molecules are carried through the column with helium. Molecules progress through the column at varying rates, arriving at the column end at different times. Arrival time coupled with the mass spectrometry provides an accurate result for molecular make up of the sample.

Lubricity. Samples were placed in an ASTM certified high frequency reciprocating rig (HFRR). A small polished metal disc (lower sample) was fixed in place of a small receptacle. When calibrating, the receptacle was filled with standard kerosene and no fuel sample. When testing, a fuel sample was added to the kerosene. A pristine metal ball (upper sample) was fixed to a reciprocating arm that moves back and forth at 60Hz. The arm was then lowered into the test sample solution where the upper ball and lower disc made contact.

A 200 gram weight was then attached to the reciprocating arm, providing a measured and constant downward force. The device was housed in a cabinet with a constant humidity and temperature. The point of contact where lower sample meets upper sample completes a circuit. The friction coefficient is then calculated using electrical resistance. The lubricity tests were 45-minutes long, during which the friction coefficient and temperature generated were recorded. At the termination of the test the ball (upper sample) was removed from the reciprocating arm and placed in a calibrated microscope attached to a computer. The area of the wear scar was then calculated using the wear scar image and processed with native software. The size of the wear scar was compared to other test samples to characterize the lubricity of the test sample.

Cloud and pour points. The cloud point of a fuel is determined by exposing a sample of fuel to gradually lower temperatures. Fuel is warmed or heated to the point where it is fluid and clear. The sample or samples are then gradually exposed to lower and lower temperatures until the fuel becomes cloudy. This test was conducted on fuel samples with a thermometer and ice bath. A fuel sample was continually stirred while the temperature was slowly lowered. The test was conducted three times.

Sandy Brae water test. The Sandy Brae water test is accurate down to 50 ppm ±20 ppm. This test measures pressure produced in a sealed container when water in a sample reacts with calcium hydride to produce gas. The fuel sample and the calcium were placed in separate chambers inside the vessel. 30 ml of fuel sample was placed in one chamber with 10 ml of reagent. Calcium hydride was placed in the other chamber. Once sealed, the vessel was shaken to mix the sample solution with the calcium hydride. Water reacts with the calcium hydride to produce hydrogen gas. The resulting pressure correlates to the ppm of water in the sample fuel.

Emissions Test Methodology

Emissions Vehicle and Instrumentation

Emissions were generated by combusting the Safou biodiesel in a 2006 VW Jetta TDI. The emissions data was collected post-catalytic converter with a Sensors Inc. Semtech-DS portable emissions measurement system (PEMS). The emissions unit is capable of measuring carbon monoxide (CO), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2), and total hydrocarbons(THC).

Emissions Data Collection

Data collection included gas concentrations for CO, CO_2, NO, NO_2, and THC. Vehicle data regarding speed, engine rpm, load, and ambient temperature and humidity were collected as well. All this data was collected, time stamped, and stored in the DS unit's removable SD card.

Pre-test procedures. The pre-emissions testing procedures included cleaning the fuel delivery system, placement of the test fuel in the tank and delivery system, and calibration of the emissions testing equipment.

Clean the tank and delivery system. The auxiliary fuel tank was emptied and wiped down with absorbent towels. The delivery system was evacuated of fuel using compressed air and the filters were replaced with new filters.

Filling the fuel line. Fuel was placed in the auxiliary fuel tank and the fuel line to the engine was removed. The key was turned to pre-ignition, turning the auxiliary fuel pump on and filling the lines with sample fuel. Once the line was filled with sample fuel, the line was reconnected to the engine fuel inlet.

Emissions equipment calibration. Equipment was calibrated prior to each test with gases of known quantity. This was done to confirm that the various analytical benches in the Semtech-DS were reading accurately across a range of gas concentrations. A pre-test calibration was done to set and confirm the unit's accuracy, and a post-test zero and span were done to confirm that the unit was reading accurately during the test. First the equipment was zeroed for CO, CO_2, NO, NO_2, and THC using ambient air. Then high ppm CO, CO_2, NO, NO_2, and THC gases were read, followed by an audit or mid-value ppm sequence of CO, CO_2, NO, NO_2, and THC.

Road test procedures.

Test route. A test course was chosen on Highway 421 east of Boone, North Carolina, between the intersection of new 421 and old 421 and the intersection of 421 and 221 (see Figure 4.7 for a map of the actual route). The length of the route was approximately five miles one way and presented several grade changes and, consequently, resulted in various loads for the engine.

Test Sequence. The Semtech-DS unit was calibrated with standard gases. Fuel was placed in the auxiliary tank following the methodology mentioned above. The vehicle was calibrated and prepared at Katherine Harper Hall and driven to the test course using petro diesel. One mile prior to the test course, the fuel delivery was switched to auxiliary fuel delivery, allowing for evacuation and stabilization of the delivery system with the auxiliary test fuel. The test vehicle was held at a constant speed of 55 mph with cruise control and braking.

Data Analysis Procedures

Data was collected by software native to the test equipment when possible. Data was otherwise recorded in two lab notebooks and then transferred to Excel for analysis and graph generation (Jaenicke, Franzel, & Boland, 1995).

Safou Data

Data regarding Safou fruit, processing, pressing yields, fuel production, calorimeter tests, fuel production, and yields were recorded in one of two lab notebooks. Data was transferred to Excel spreadsheets to aid in processing and generation of graphs.

Calorimeter Data

Calorimeter data was collected in a notebook and then processed using Maple 13 based software in order to calculate temperature change. This data was then corrected using the methods described in an earlier section, and data analysis was completed in Excel.

Emissions Post-test Data Processing

Data was uploaded from the Semtech-DS unit as an .XML with Semtech PC software. This data was post-processed using the Semtech PC software and outputted as a .CSV file which could be opened with Excel. Data from various tests fuels were then compared and graphs generated using Megatron software written by fellow graduate student Eric Urban.

CHAPTER 4

RESEARCH FINDINGS AND RESULTS

Introduction

The research findings are organized into three main sections: Fruit and Oil data, Fuel Characteristics data, and Emissions data. The Fruit and Oil section addresses all of the steps required from harvesting of the fruit through drying and pressing for oil, and includes a section detailing the energy requirements for Safou oil production. The Fuel Characteristics section details the composition of Safou biodiesel and analyzes its fuel characteristics in relation to ASTM specifications. Finally, the Emissions data section describes the results of the emissions tests conducted, comparing Safou emissions to those from soy biodiesel and petro diesel.

Fruit and Oil

This section includes the data collected during my visit to the DRC in January 2010 for the purpose of harvesting Safou. As is pointed out in the limitations of the study section this data set is small, so a generalized conclusion cannot be derived from it. However, there is sufficient information to place Safou harvesting in context and to provide some insights into its relevance as an energy crop.

Harvesting

Safou fruit was harvested from nine trees with varying physical characteristics. Fruit was harvested on the grounds of the Centre Évangélique de Coopération (CECO) campus in

Kimpese. Students at the CECO school were asked to participate in the harvesting of fruit. Students are typically discouraged by the groundskeepers from picking fruit from the trees, but this was an opportunity for them to pick the fruit for this research with the added bonus of getting some sought-after fruit. The grounds have several dozen mature trees ranging from 3 to 25 meters in height. As mentioned previously, the fruiting season was late so the harvesting was limited to the trees that had ripe fruit and the smaller trees from which students were able to pick safely. The fruit was harvested on January 15, 2010 between 10:30 am and 2:00 pm. During that time nine trees yielded 75.5 kilograms of ripe and near-ripe fruit. In general, one person went up the tree and picked fruit by hand, if possible, but more frequently a stick with a hook at the end was used to dislodge the fruit. Fruit was allowed to drop to the ground with little care taken to avoid bruising. The first tree that was approached was laden with fruit and yet had lost much of its foliage. Three male students were able to climb this tree at the same time. It was relatively low to the ground and yielded ~40 kilograms of fruit in a half hour of picking time.

Fruit sample inclusion criteria.

Ripe fruit. Fruit was considered usable for our sample if it was considered ripe enough to eat. Within this "ripe enough to eat" category the fruit was sorted into near-ripe and ripe fruit based on the extent of purple pigment evident on the fruit. Fruit with 95-100% purple was considered ripe and anything between 80%-95% was considered near-ripe. Of the ~250 kgs of fruit collected for the sample, approximately 50 kg was near-ripe.

Spoiled fruit. Fruit was collected in Kimpese, placed in used onion bags, and transported by car to the campus of The American School of Kinshasa (TASOK) for processing. After transport to TASOK, at the beginning and end of each day spoiled fruit was culled from fruit that had not yet spoiled. Spoiled fruit was any fruit that had begun to go soft, was easy to deform, and had an outer skin that was easily broken. This spoiled fruit was processed separately.

Fruit characteristics. A sample of 27 fruits were cut in half, the seeds removed, and the seed cluster membrane separated from the pulp. The three parts were then weighed using a triple-beam balance with accuracy to the tenth of a gram. The results in Table 4.1 summarize the average weights of 25 fruits and their constituent parts. Two fruits that varied considerably from the other 25 fruits were removed from the data set. The results are found in Table 4.1.

Table 4.1
Comparison of Whole Fruit, Pulp, Seed Cluster, and Seed Membrane Based on Percentage of Total Weight

Fruit	Pulp	Seed Cluster	Seed Membrane
100.0%	75.6%	23.8%	0.7%
±0.04	±0.05	±0.03	±0.1

Fruit Processing

Fruit processing was not a primary focus of this research but observations of what the process could do to the fruit pulp were conducted and the implications for oil extraction were examined. This information is pertinent regarding future development of Safou as a crop for oil extraction. The processes summarized below are meant primarily to present how the pulp was processed in order to harvest the oil. Energy inputs as they pertained to processing the oil for this study were documented where possible, and several obstacles to processing Safou for oil extraction were indentified in terms of energy inputs required. The primary goal of this section is not to identify and quantify best methods for processing, but to inform how oil for this research was attained and what may need to be improved upon for future viability of Safou as an energy crop.

Decorticating the fruit.

Ripe fruit. Fruit, including the seed cluster, was cut in two. Each half of the seed cluster was scraped out using a spoon. The halves were then sliced using knives and mandolins into pieces between 1/16th inch and 1/4 inch to expedite drying. A processing time trial was undertaken with three people and 60 kg of fruit. It took three people 4.5 hours to decorticate and chop 60 kg in preparation for drying. The result of the methods employed for this test resulted in an hourly rate of 4.44 kg of fresh fruit per individual.

Spoiled fruit. Spoiled fruit included fruit that had lost the integrity of the outer pulp. Pulp was easily scraped from the central seed cluster using one's fingers or a spoon. The soft and mushy pulp was then spread out on dehydrator trays or placed in oven tins for drying. No pulp removal time trials were undertaken; however, it was apparent to those who had done the 60 kg of the unspoiled fruit that dealing with each fruit required less time, particularly because there was no chopping involved prior to drying.

Pulp-seed water separation test.

Ripe fruit. This test included splitting a fruit in half and, without removing the central seed, chopping both halves into 1/4" strips across the fruit. The chopped pieces of fruit were then tumbled in a jar to help separate pulp from seed. The seed and pulp pieces were then poured in a glass with water in it. The ripe fruit that retained its integrity would float along with the outer membrane of the seed cluster. The seeds would sink. This process could be incorporated for large-scale separation of fruit pulp after being mechanically chopped.

Spoiled fruit*.* This test included taking the spoiled fruit and simply placing it in the bucket and agitating the water. The spoiled fruit would sink while the seed cluster with its uncompromised membrane would float. This method of pulp removal would only be useful if enzymatic processing, mentioned previously in Chapter 2, is productive in water.

Fruit Drying

Dehydrators. Fruit was dried in preparation for pressing. Initial drying was done with dehydrators to establish a target end point based on a percentage of the fruit's starting weight. Dehydrator trays were weighed on a balance accurate to a tenth of a gram. Each was labeled with a number and its tare weight. Fruit pulp was then placed on each tray in equal quantities. The dehydrator used for this test was a 350-watt Oster brand dehydrator. The trays were stacked sequentially with tray one on the bottom. The bottom tray was then removed and placed on the top after each weighing, in order to promote a more even drying. This was done because the dehydrator used for this test had an updraft design and the bottom tray would dry faster than trays above it. Figure 4.2 shows how the Oster trays began at a common weight and also shows that weight change differed based on the bottom-to-top rotation. Bottom trays lost more weight relative to other trays except when no more weight loss was possible. Figure 4.3 shows the average weight of the trays at the five points with a trend line suggesting the path of the drying curve. Actual drying curves for this material would require more evenly spaced data points. Figure 4.3 is only meant to demonstrate what that drying curve might look like. It is interesting to note that the Onesco dehydrator had a downdraft design and even though the trays were rotated bottom to top the difference in tray weight was less, suggesting a more even drying. Several drying tests were conducted out to

17 hours and the dry weight appeared to stabilize between 30-34% of the starting wet weight. This percent wet weight was the targeted range to determine when pulp had been sufficiently dried in the dehydrators or in conventional ovens. Dehydrator temperature ranged between 130-155° F, depending on the model and settings. Temperatures for conventional kitchen ovens ranged from 250-300° F, and the majority of pulp was processed in conventional kitchen ovens below 250°F.

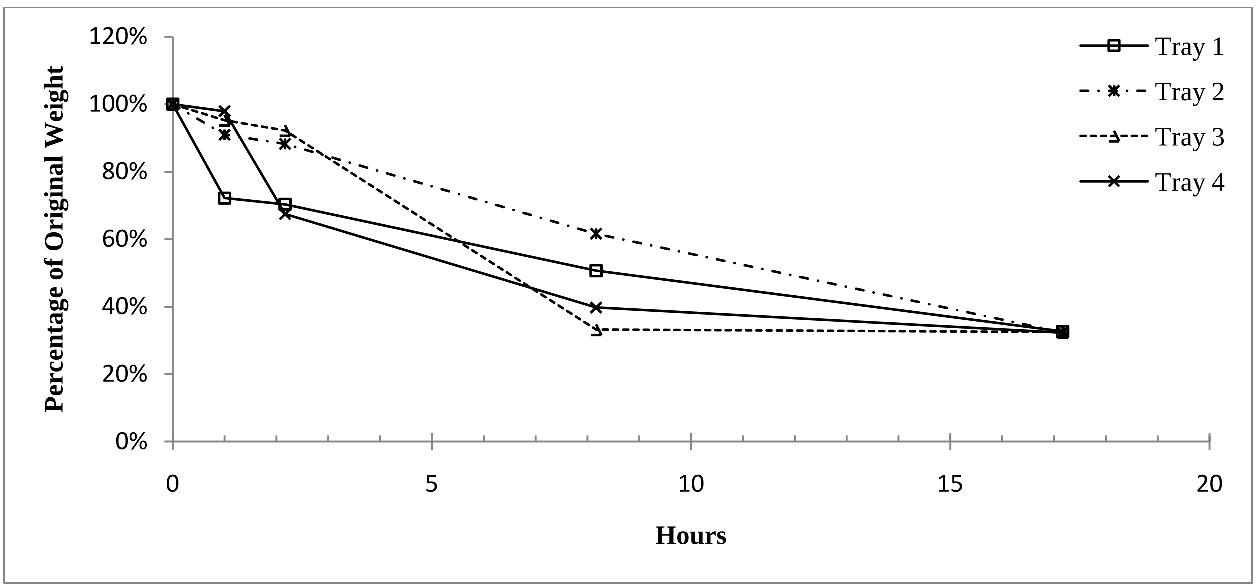


Figure 4.1. Percent weight loss for four Oster dehydrator trays being rotated from bottom to top after each weighing.

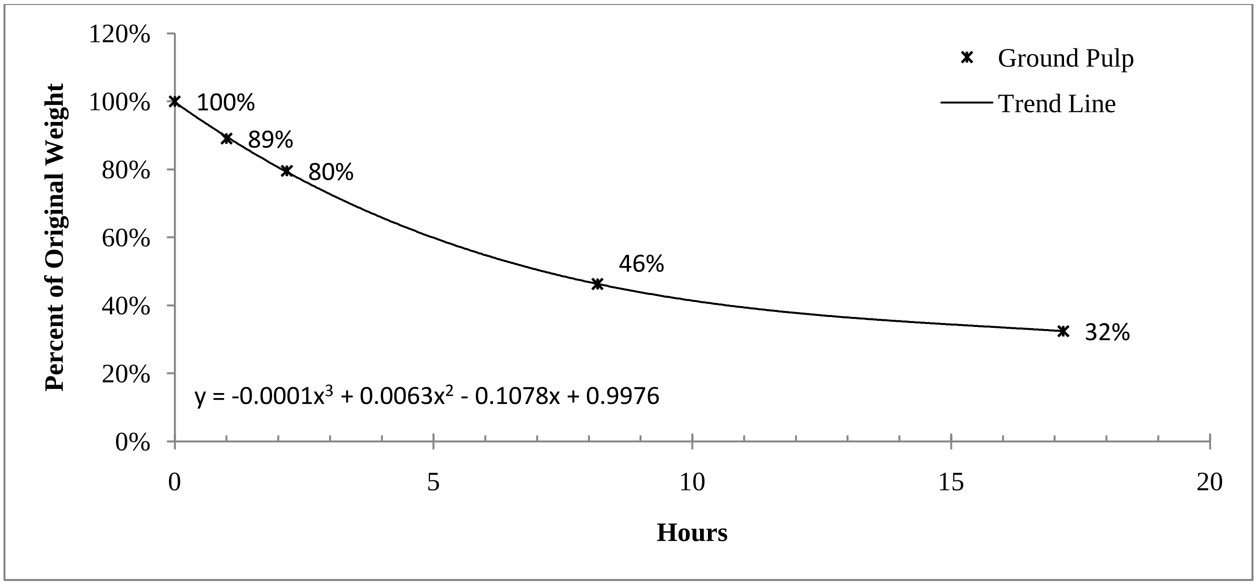


Figure 4.2. Average of trays from Figure 4.1 with a trend line used to help describe the progression of moisture removal.

Oven drying. Chopped fruit pulp was placed in baking tins and placed in conventional kitchen ovens. Temperatures were set at 250° F and the oven doors propped open with the handle of a wooden spoon to allow hot moist air to escape and cool air in. Oven thermometers in various ovens showed temperatures ranging from 250°F to as low as 220°F. Trays were stirred and rotated every 30 minutes. Drying was considered done when the pulp was brittle and when weighing the dried pulp confirmed that more than 62-64% of the starting weight had been removed. During cooling pulp lost as much as 1-2% of its weight, culminating in a range of total wet weight removed of 63-66%.

Energy for drying. Three dehydrators were used for the dehydrating process. These included an Oster®, a Magic Chef®, and an Onesco®. Each dehydrator varied in terms of power, number of trays, and updraft or downdraft capabilities. Table 4.2 shows primary characteristics of each model.

Table 4.2
Dehydrator Specifications

Model	Wattage	Trays	Forced Draft
Oster®	350	4	Up
Magic Chef®	250	5	Up
Onesco®	500	4	Down

The listed power and time required to reach terminal drying weight was used to calculate energy required per gram of fruit dried. Data from the Oster®, Magic Chef®, and Onesco® dehydrators were collected. Watt hours per kilogram dry pulp (Wh/kg_{dry}) were as low as 6000 Wh/kg_{dry} with a range between 6-7 kWh/kg_{dry}. A summary of the equation used for calculations is shown in Figure 4.3. Some tests exceeded this number due to the increased time allowed in the dehydrator in order to determine a terminal drying percentage. This of course used more energy than was necessary to arrive at the drying point. No energy data were collected for oven drying.

Figure 4.3 Equation for drying energy consumption per gram of dried fruit pulp.

Processing Effects on Fatty Acid Content

Dehydrator and oven-dried pulp. Dehydrator temperature ranged between 130-155° F, depending on the model and settings. Temperatures for conventional ovens ranged from 250-300° F. Titrations of the oil showed that oil that had been extracted from dehydrated pulp was below 1 g^{KOH}/liter, while oil that had been roasted titrated in excess of 5

g^{KOH}/liter. Lower drying temperatures are ideal for preserving quality of oil and perhaps in terms of energy use. However, no data was collected to confirm oven energy consumption in order to compare the two drying methods.

Pressure-canned pulp. Wet pulp and fruit were pressure-canned at 250° F and later dried in the United States in a conventional oven set to 210° F with the oven door cracked. Oil extracted from this pulp also titrated below $1g^{KOH}$/liter.

Pulp Pressing

The press. The press used for oil expression was a Taby 20® with a maximum power rating of 600 watts. Due to varying speed and an unrated heating collar set to maintain a temperature range, a Watts-up? Pro® meter was used to collect energy data during press operation.

Press and heated-collar loads. Figure 4.4 shows the press load including time prior to pulp being pressed as well as cool-down time. The square segments found before and after the pressing represent the load from the heated collar. This load also explains the sudden surges in the overall load profile.

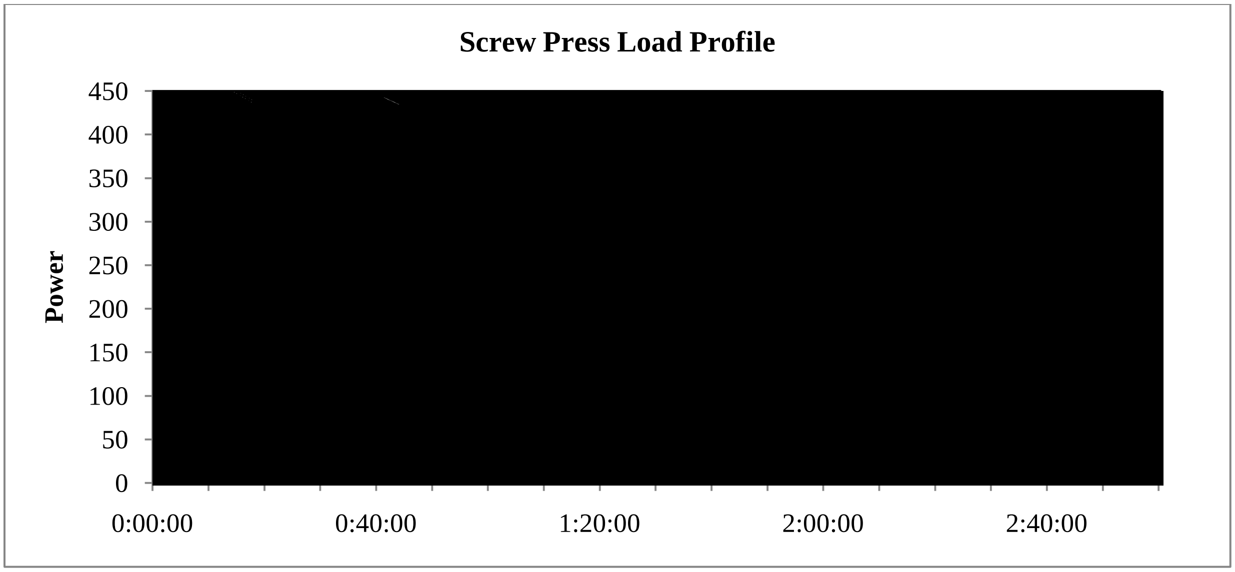


Figure 4.4 Screw-press load profile during the extraction of 8.245 kg of dried pulp.

Pressing yields for raw oil. Raw oil press yield was calculated by dividing raw oil weight by the initial dry pulp weight. After settling, neat oil was decanted and proved to be 88% of initial raw oil values. Results for pressing and settling yields are summarized in Table 4.3.

Table 4.3

Screw Press Efficiency Based on Dry Pulp Weight to Unsettled Oil Weight

Dry Pulp (g)	Press Cake (g)	Oil (g)	Cake + Oil % Start Wt.	Raw Oil % Dry Wt.	Neat Oil[c] % Dry Wt.
774	326	420	0.96	56	49
775	358	496	1.10[a]	58	51
1492	696	798	1.00	53	47
572	256	306	0.98	54	48
765	367	388	0.99	51	45
921	422	493	0.99	54	48
753	337	409	0.99	55	48
700	327	364	0.99	53	47
729	366	375	1.02[b]	51	45
764	349	395	0.97	53	47
		Averages			
824.5	380.4	444.4	1.00	54	47

[a,b] This over unity is indicative of samples that required moisture added during pressing.
[c] This value was calculated as 88% of Raw Oil, a value established from several settling samples.

Oil settling. In order to get a number for neat oil extracted, raw oil samples were heated to 175° F and allowed to settle for more than eight hours. They were then agitated for a minute to suspend all precipitates and a sample poured into a 100 ml graduated cylinder. The cylinder was then placed in an oven at 175° F for more than 15 hours. The precipitates, or "foots," were recorded in ml. Results are found in Table 4.4. The majority of oil used for the test fuel had an average of 12 ml of foots, and this value is used for overall yield data. It is interesting to note that dehydrated spoiled fruit had the lowest value of sediment and near clarity was achieved in less than half an hour. Non-spoiled pulp oil settled clear overnight, but oven-roasted pulp that had experienced excessive temperatures (>300° F) still had a substantial amount of pulp suspended in the oil.

Process heat and acid values. Five oil samples were titrated over the course of this research. The samples shown in Table 4.4 are organized by titration values in the far right column. The test fuel was a mixture of all oil samples and was heated and centrifuged to produce neat oil. It appears that drying heat in excess of 250° F appears to correlate with higher titration values. Neat oil heated to 205° F does not necessarily cause a breakdown of triglycerides-producing free fatty acids; however, oil in the pulp is in proximity to water and other pulp material which may increase the effect of temperature on oil acid values.

Table 4.4
Comparison of Oils in Terms of Pre-press Processing, Sediments, and Titration Values.

Pulp State	Pre-Pressing	Drying Temp. (F)	Percent (wet/bases)	Foots (%)	Titration (g^{KOH}/l)
Ripe	Canned/Dried	210	32-34	-	< 0.2
Ripe	Oven Dried	200-250	32-34	12	0.02 < 3.01
Spoiled	Dehydrated	120-155	32-34	8	< 3.01
Ripe	Over roasted	>300	32-34	31	> 5.5
Ripe	Dehydrated	120-155	32-34	23	-
Various[a]	Mix	120-300	32-34	-	5.27

[a] Represents the titration of the oil feedstock used for the test fuel which was a mixture of various oils.

Energy for pressing.

Figure 4.5 shows the segment from Figure 4.3 in which pulp was being pressed. The power load and total cumulative energy is indicated as well. This energy yield is specific to the Taby 20® and Safou pulp used for this study. Energy requirements are calculated by dividing energy consumed by oil yield (i.e., Wh/[pulp weight · percent yield]). In the example of Figure 4.4 the calculation would be 258 Wh ÷ (8.245 kg · 47%) = 67 Wh/kg. This press efficiency is higher than some reported industrial press efficiencies ranging between 36-41 Wh/kg (Okoye, Jiang, & Hui, 2008).

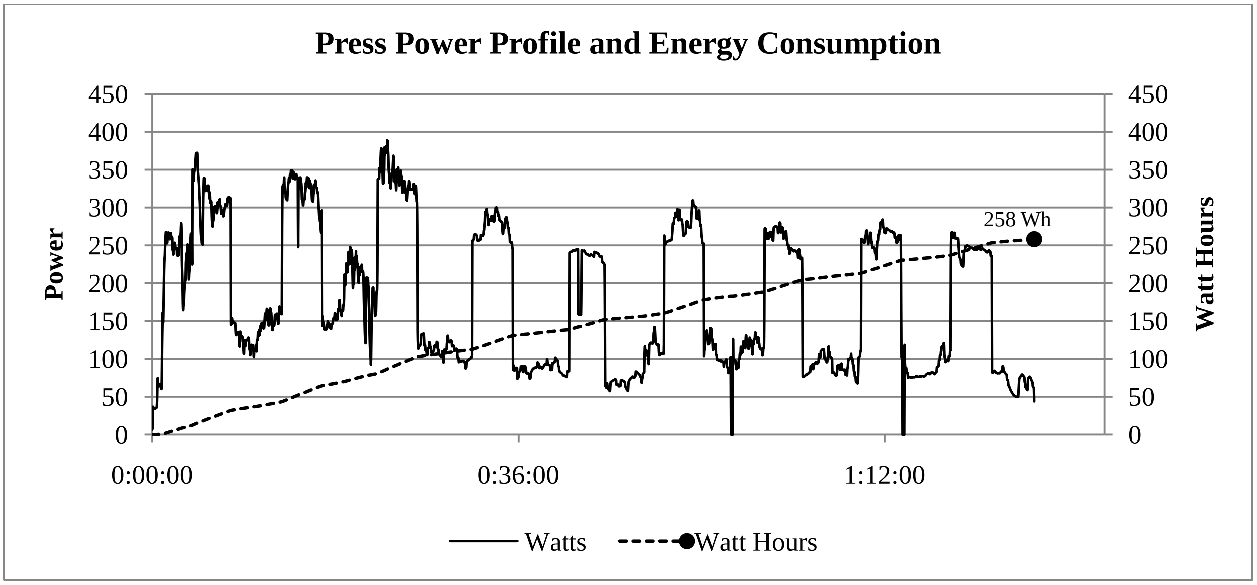


Figure 4.5 Cumulative energy for the pressing of 8.245kg of dried pulp.

Energy Densities

The energy density of Safou FAME, Safou oil, press-cake, and seed were determined using an oxygen bomb calorimeter. Standard procedures for calibration and corrections for iron combustion and acid production were performed per the instructions of the Parr Oxygen Bomb Manual. FAME and oil did not require corrections for endothermic acid reactions. Press-cake and seed experiments did test positive for acid creation. Results are summarized in Table 4.5.

Table 4.5
Summary of the Energy Content of 'Safou Oil, Press Cake, Seed, and Safou-derived FAME

Sample	Energy	Unit
FAME	20.632	kJ/g
Oil	19.894	kJ/g
Press-Cake	15.175	kJ/g
Seed	11.587[a]	kJ/g

[a] Value was not corrected for acid production but titration results were less than press-cake values and acid corrections of 0.9 kJ/g.

Energy Calculation for Safou Oil Production

Energy needed for oil production was calculated by summing the total energy required for drying and pressing. The overview of the calculation used for pressing energy per kilogram of neat oil is shown below in Figure 4.5. The average raw oil percent (54%) was corrected for the average percent of oil (88 ml/100 ml) that was neat when foots had settled. This established a 47 % neat oil pressing efficiency based on dry weights. This percent was multiplied by the total dry pulp weight pressed: $47\%^{\text{raw oil}} \cdot 8.245\text{kg}^{\text{dry pulp}} = 3.875\text{kg}^{\text{neat oil}}$. The energy required to press the oil was then divided by the weight of the neat oil.It was established previously that drying required 6000 Wh/kg . Figure 4.6 summarizes the equation for total energy required to produce a single kilogram of Safou oil. The methods used for this research resulted in a total energy requirement of 6060 Wh/kg: 6000 Wh/kg + 67 Wh/kg = 6067 Wh/kg. The ratio of process energy when compared to the energy density of the oil is 1.09:1. This ratio is negative, which in terms of energy production of the oil alone would disqualify Safou as a biofuel feedstock. Although this energy balance is unfavorable, energy values recorded for this research are not indicative of potential energy balance because of the processing methods used for this small sample. A potential scenario is outlined in Chapter 5 using reported Wh/kg for drying and pressing.

Figure 4.6 Equation for press energy consumption per gram of clean oil fruit pulp.

Figure 4.7 Equation for total energy consumption per gram of clean oil fruit pulp.

Fuel Characteristics of Safou

Safou Biodiesel Characteristics

Several biodiesel transesterification reactions were done in an effort to produce fatty acid methyl esters (FAME) from Safou oil. Lab-scale reactions produced yields greater than 80%, whereas larger-scale reactions—in particular the two-stage acid-base reactions for final fuel production—proved to be incomplete. Bench-top testing showed potential test fuel reaction yields above 85% by volume, while the final fuel reaction resulted in a 50% yield. This reduction in yield is likely due to the methods used for the five-gallon reaction vessel as well as to temperature variations during reaction. Furthermore, the use of NaOH created solid glycerin which, when heated and reacted with phosphoric acid to precipitate salts and glycerin, showed a 40% by volume FFA content.

Safou Oil Feedstock Composition

High yield reactions were used to determine molar ratios of the raw oil. Composition was determined after successful conversion to FAME with a GC/MS. Several compositions of Safou oil have been reported from previous literature (see Table 2.2). Table 4.6 shows the results from the GC/MS performed on this study's samples of Safou biodiesel. The first sample was produced from oil that had been extracted from pressure-canned and dried fruit pulp. The second sample was fuel produced from a mixture of oil extracted from pulp that had been dehydrated as well as oven dried and was the oil used for fuel production. The third sample was oil from spoiled fruit pulp that had been dehydrated.

Table 4.7

Summary of ASTM 6571-09 Tests Performed on the Safou Fuel

Table 4.6

Carbon Chains Found in Safou-Derived Fatty Acid Methyl Esters With Varying Pre-Press Feedstock States and Transesterification Reactions

Side Chain Double Bonds	**C-13**	**C-16**	**C-16 (1)**	**C-17**	**C-18**	**C-18 (1)**	**C-18 (2)**	**C-18 (3)**	**C-20**	**C-20 (1)**
$Safou^{BD}$	0.24	**35.59**	0.46	0.27	-	**35.53**	**24.90**	2.14	0.42	0.33
$Safou^{TF}$	-	**43.41**	-	0.21	-	**15.07**	**32.88**	-	0.29	0.28
$Safou^{Sp}$	-	**42.52**	-	-	3.39	**17.48**	**35.05**	-	0.25	0.26

Property	**Method**	**Limits**	**Units**	**Analysis**	**Pass/Fail**
Flash Point (*closed cup*)	ASTM D 93	93 min.	C°	149	Pass
Kinematic Viscosity, 40 C	ASTM D 445	1.9 - 6.0	mm2/sec.	4.938	Pass
Copper Strip Corrosion	ASTM D 130	No. 3 max.		1a	Pass
Cloud Point	ASTM D 2500	report	C°	12.8	Report
Acid Number	ASTM D 664	0.5 max	mg KOH/g	1.262	Fail
Free Glycerin	ASTM D 6584	0.02 max.	% mass	0.0001	Pass
Total Glycerin	ASTM D 6584	0.24 max.	% mass	0.334	Fail
Oxidation Stability	EN 14112	3 min.	hours	2.59	Fail
Lubricity, HFRR at 60°C	ASTM D 6079 [a]	520 max.	microns	434	Pass
Moisture	Karl Fischer	500 max	ppm	814	Fail

[a] Lubricity test was performed on $Safou^{BD}$ (Table 4.6) while all other tests were performed on Safou BD Fuel.

Safou Fuel Analysis

Safou oil and fuel characterization is summarized in Table 4.7. The table does not represent the entire battery of tests required for ASTM 6751-09 certification (see Table 2.7 for a complete list of tests required for ASTM certification). Analysis showed that Safou fuel produced for these tests did not pass all criteria in the ASTM specifications. Actual results are indicated in the Analysis column with a “pass” or “fail” rating. Strictly speaking, the Safou test fuel cannot be termed ASTM-certified biodiesel; therefore, the more general term *Test Fuel* has been adopted.

Emissions Test Results

Course and Conditions

The course selected for this test was a segment of Highway 421 east of Boone, NC. Figure 4.7 gives an overview of the course and turnaround points. Figure 4.8 shows course elevation changes. Emissions tests were all performed on November 1, 2010. Ambient temperature was 55° F and relative humidity was at 42%. The test for emissions was done in a sequence of Petro, Soy, Safou, Petro, Soy. Soy and petro runs chronologically adjacent to the Safou run were used for emissions comparisons. Course, run duration, vehicle speed, and ambient conditions were consistent between compared test runs with the assumption that the same amount of work was performed by each fuel.

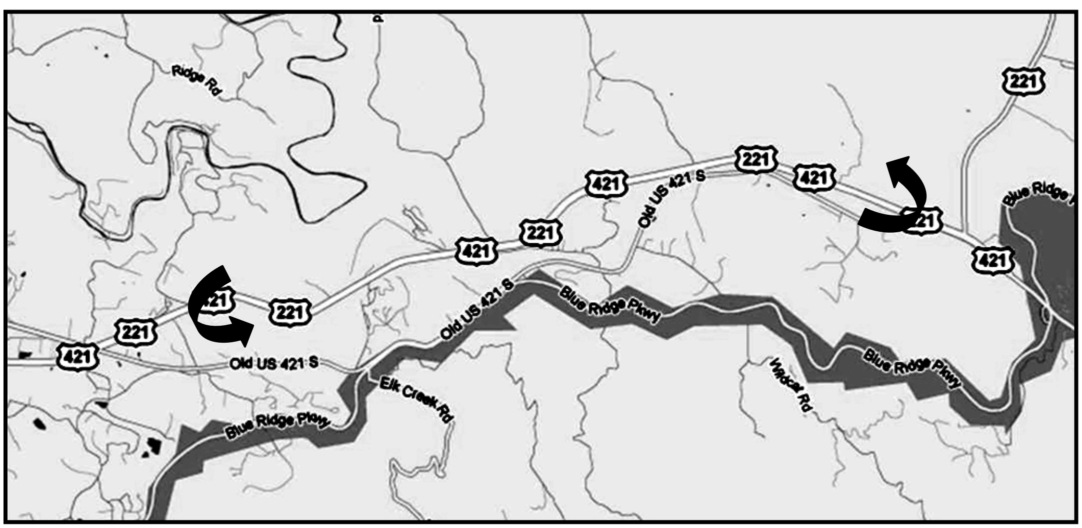


Figure 4.8 Map of course used for emissions testing.

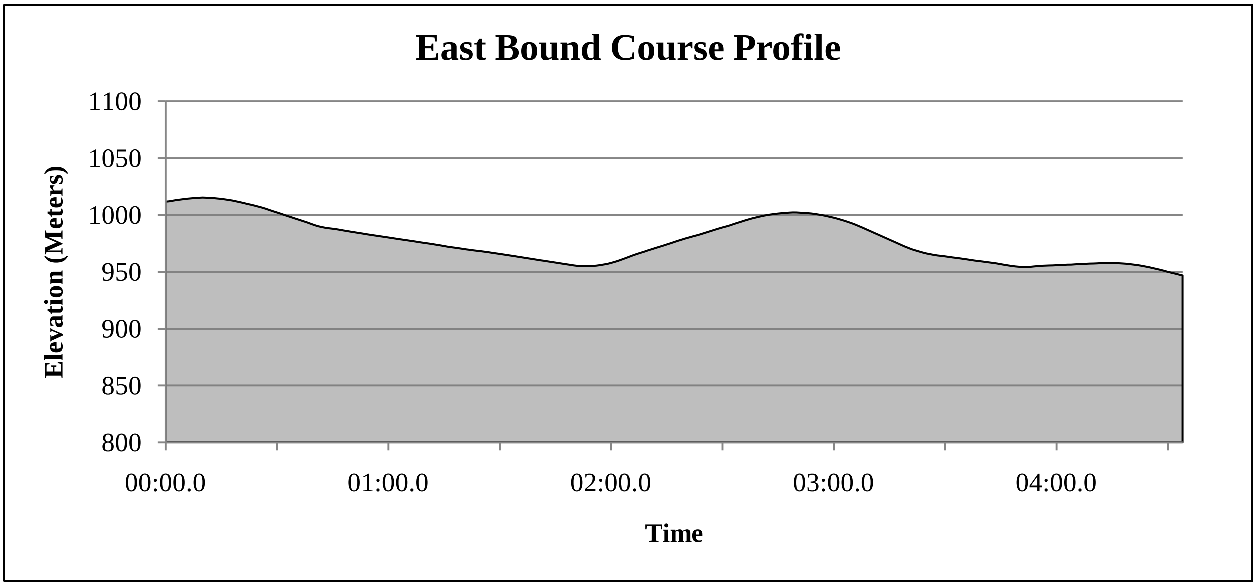


Figure 4.9 East-bound emissions course profile: Elevation in meters.

Fuel Sample Change Procedure

The auxiliary tank and fuel line, including the fuel cooling loop, were purged between test fuels. Each fuel had a unique fuel filter that was changed after purging was complete. The tank was wiped clean with shop towels after each fuel run in preparation for the next fuel. The auxiliary fuel pump was then turned on to fill the fuel line, including the cooling loop. Fuel was allowed to flow through the line for several seconds to help flush the line.

Emissions Data Collection Equipment

Emissions data was collected using a Semtech-DS® portable emissions measurement system produced by Sensors, Inc. The Semtech-DS has several gas analyzing benches including a flame ionization detector (FID) for total non-methane hydrocarbons (THC), a non-dispersive ultraviolet (NDUV) bench for NO and NO_2, as well as a non-dispersive infrared (NDIR) bench for CO, CO_2 and HC. Benches were calibrated using ambient as the zero. Span (high ppm) and audit (low ppm) gases were used to calibrate the various gas analyzers over a range of concentrations. Table 4.8 summarizes the accuracy of the Semtech-DS unit for testing emissions.

Table 4.8
Accuracy of Semtech-DS Analytical Benches

Analyzer Bench	Gas	Range of Measurement	Accuracy	Resolution	2 Hour Drift
FID	THC	0 – 100 ppmC	2.0 % of reading or ±5ppmC whichever is greater	0.1 ppmC	±5ppmC
NDIR	CO	0-8%	±3 % of reading or 50ppm, whichever is greater	10 ppm	±50ppm
	CO2	0-20%	3 % of reading or ±0.1%, whichever is greater	0.01%	±0.1%
NDUV	NO	0 to 3,000 ppm 0 to 900 ppm 0 to 300 ppm	2 % of meas. or 2 % of pt[a]	0.1 ppm	≤10ppm
	NO2	0 to 500 ppm 0 to 300 ppm 0 to 100 ppm	2 % of meas. or 2 % of pt[a]	0.1 ppm	≤10ppm

[a] "pt" refers to the overall flow-weighted mean value expected at the standard. "Meas" refers to the actual flow-weighted mean measured over any test interval.
Note. Adapted from Semtech-DS User Manual by Sensors Inc, 2010,p. 230-231,

Flow Calculation for Emissions Data

Due to a recent software upgrade to the Semtech-DS, certain defaults were reset including the selection for the flow meter. Consequently, exhaust flow had to be indirectly calculated for emissions data. Calculations for the exhaust flow, which allow for a calculation of actual mass of emissions, were produced following the outline of the equations listed below. This method assumes the conservation of mass where molecular mass of emissions will equal the molecular mass of air and fuel going into the cylinder. Equation one addresses the molecular mass of the air going in and the second equation deals with the mass of fuel. The third equation multiplies the sum of equations one and two by the instantaneous gas concentrations recorded for that data point. A fourth equation was required to covert g/s to g/mi with the use of data specific speeds.

(1)

(2)

(3)

A comparison of calculated data versus data collected with exhaust flow meter values showed an acceptable distribution for a comparison of fuels. Figure 4.9 shows the distribution for total emissions from petroleum diesel on a day with similar conditions as that of the test data.

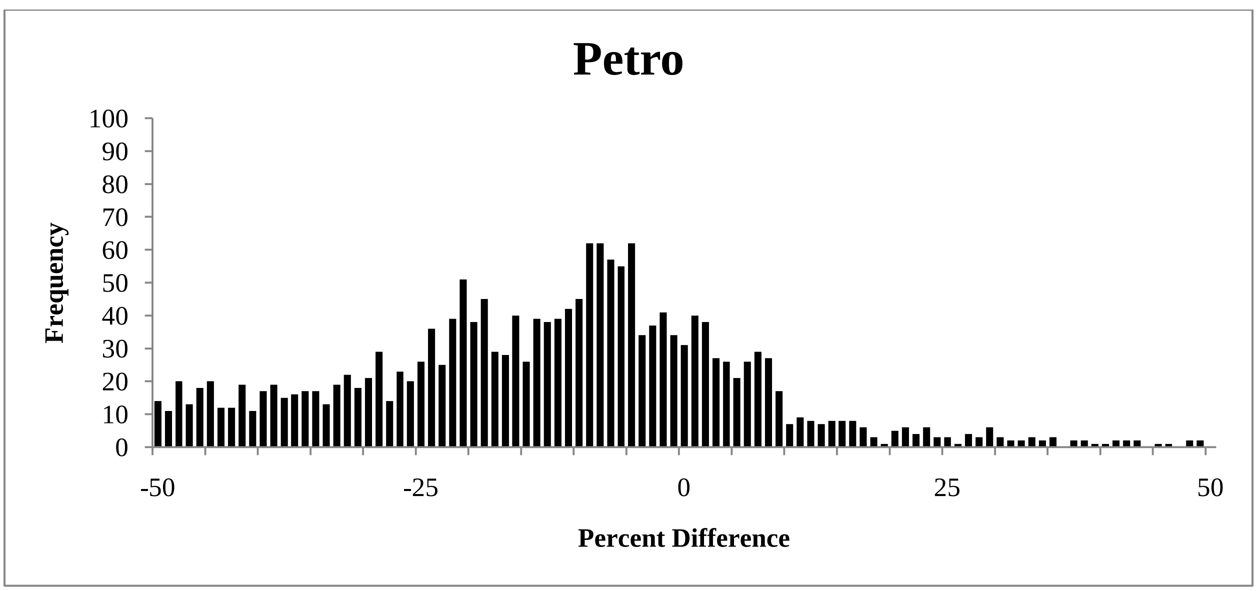


Figure 4.10. The distribution percent difference between measured data and calculated data for petroleum fuel.

Figures 4.10-4.14 were generated with g/s data that was generated using the above equations. In each pair the left graph is always petro versus Safou, while the right side is soy versus Safou. These initial comparisons do show some structure in their characterizations of emissions from the different fuels. For instance, in Figure 4.10 there is a sudden increase in CO_2 for soy and Safou at 50% engine load. This is clear from the stratified cloud and correlating gap in the main body of data points just below it. While these figures are useful in doing initial comparisons, it became apparent that comparing fuels after binning data according to engine load would perhaps provide data sets for each fuel that would be more readily comparable. Initially this comparison was done for grams per second data, as is shown in Figures 4.15-4.19. The same method of binning data according to engine load was applied to calculated grams per mile data, where the analysis used g/s data over the course of a mile. These findings are shown in Chapter 5.

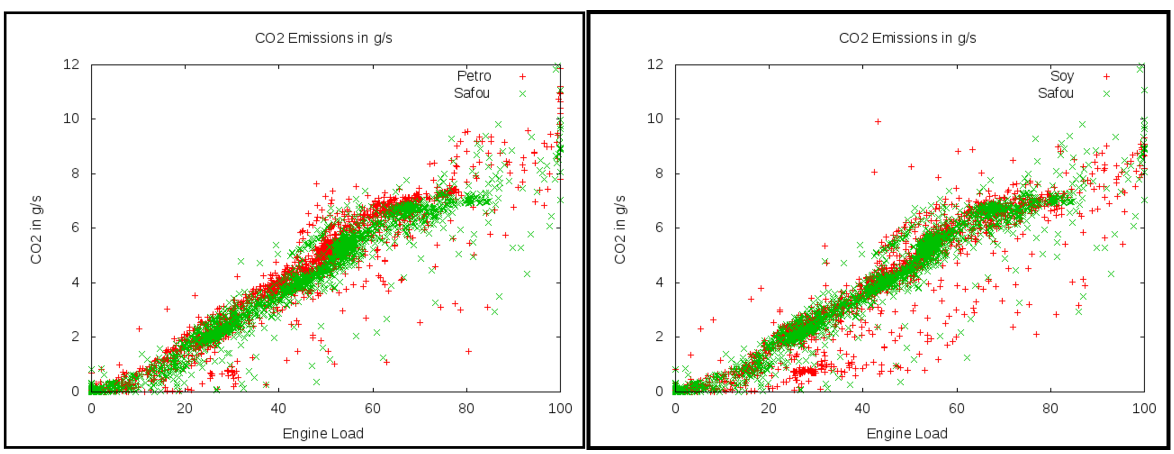


Figure 4.11. CO_2 emissions vs. engine load for petro and Safou and for soy and Safou

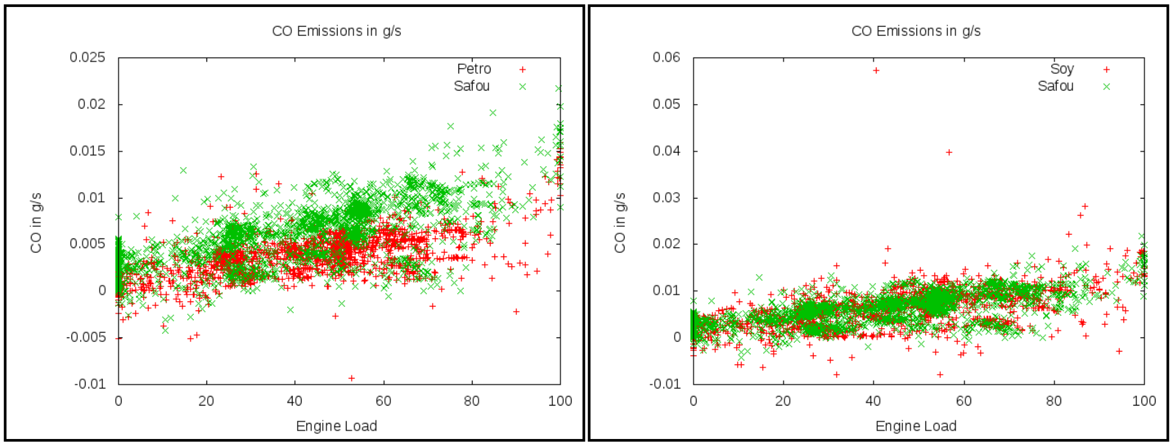


Figure 4.12. CO emissions vs. engine load for petro and Safou and for soy and Safou.

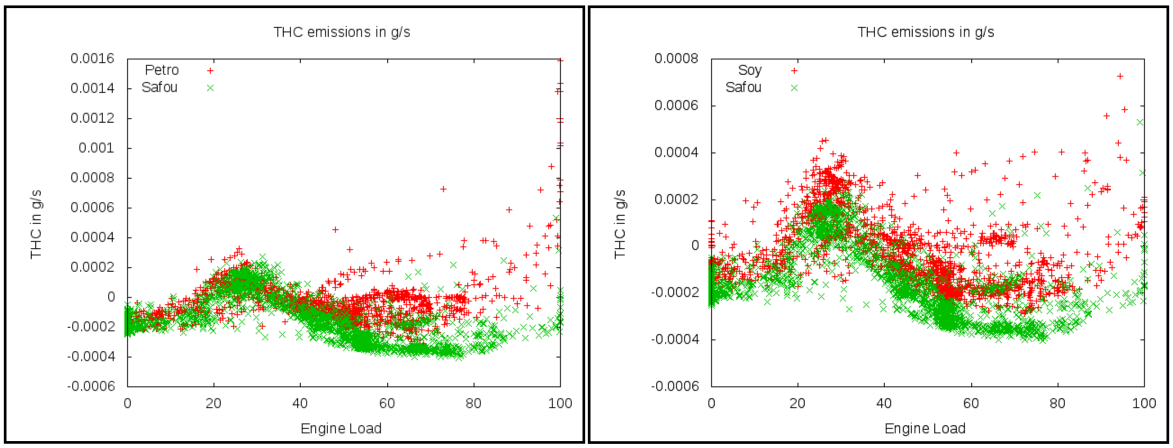


Figure 4.13. THC emissions vs. engine load for petro and Safou and for soy and Safou.

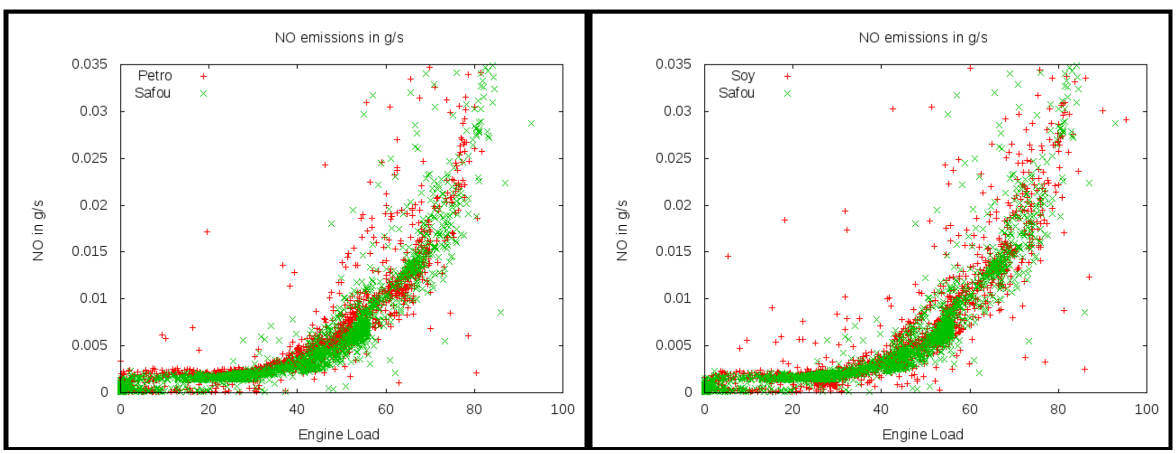
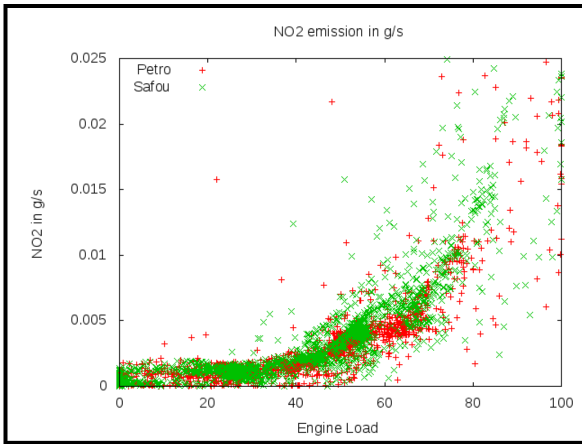


Figure 4.14. NO emissions vs. engine load for petro and Safou and for soy and Safou.



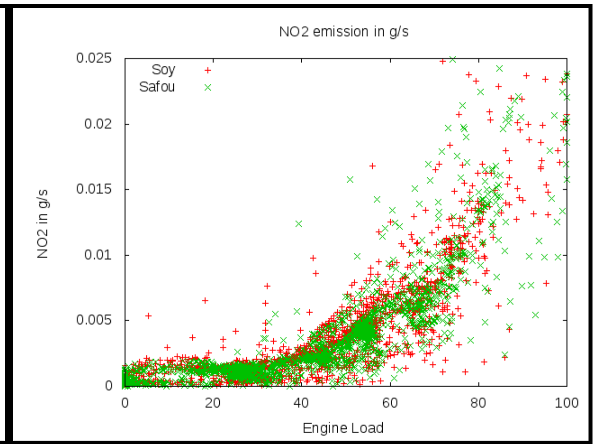


Figure 4.15. NO_2 emissions vs. engine load for petro and Safou and for soy and Safou.

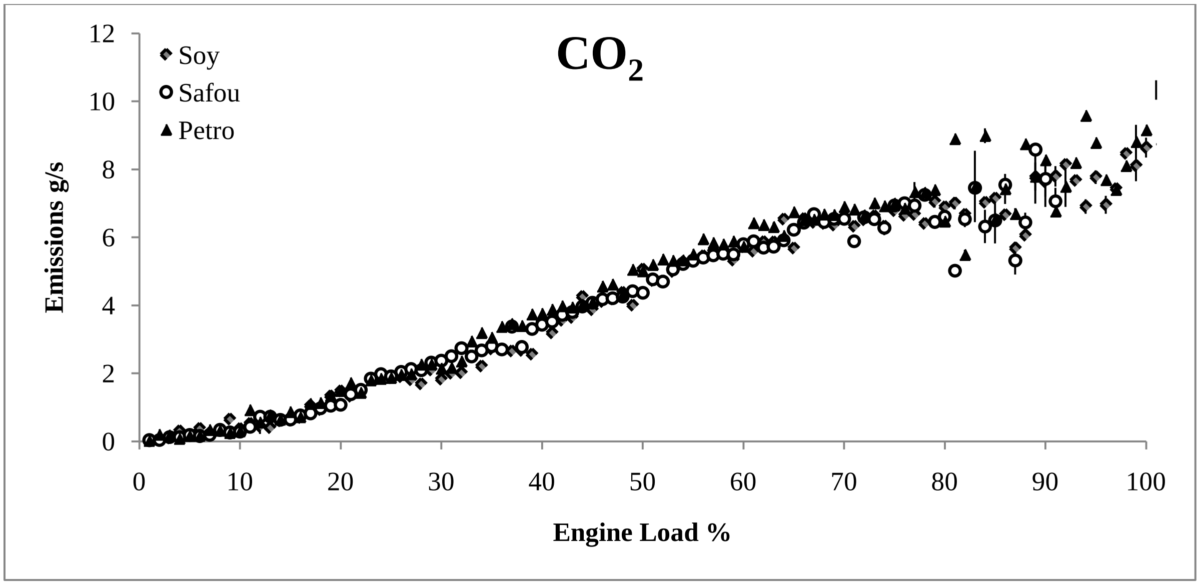


Figure 4.16. CO_2 (g/s) emissions from Safou vs. petro.

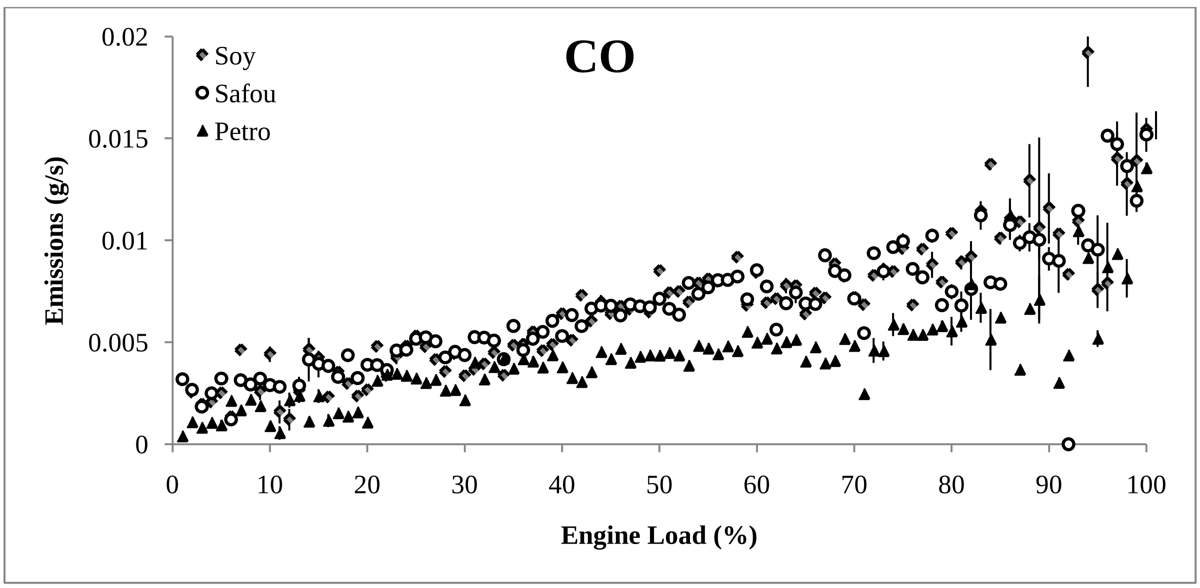


Figure 4.17. CO (g/s) emissions from Safou, soy, and petro.

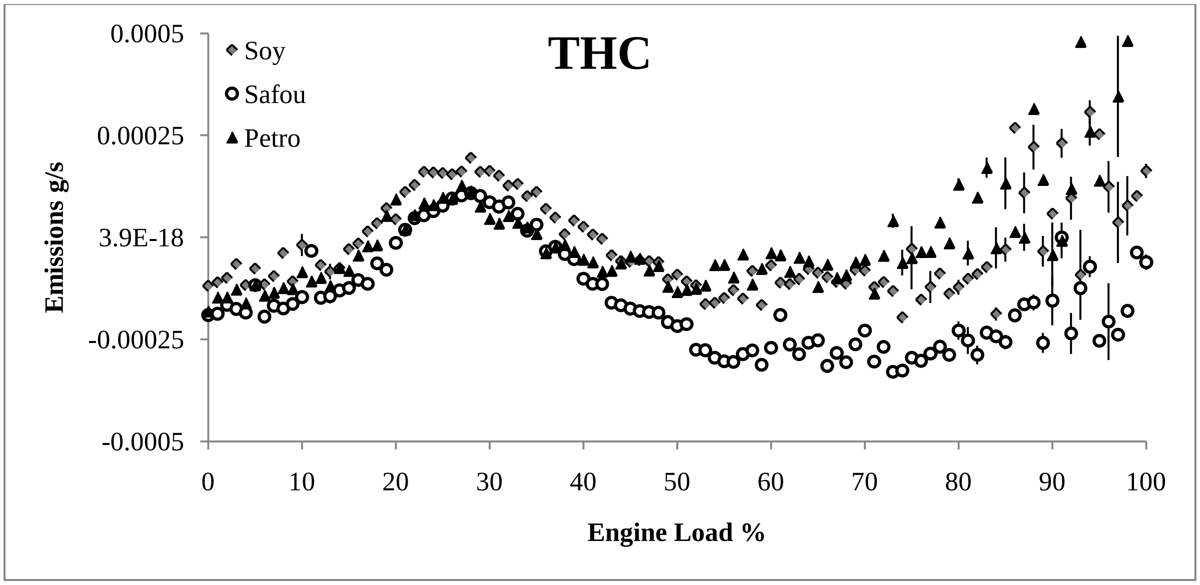


Figure 4.18. THC (g/s) emissions from Safou, soy and petro.

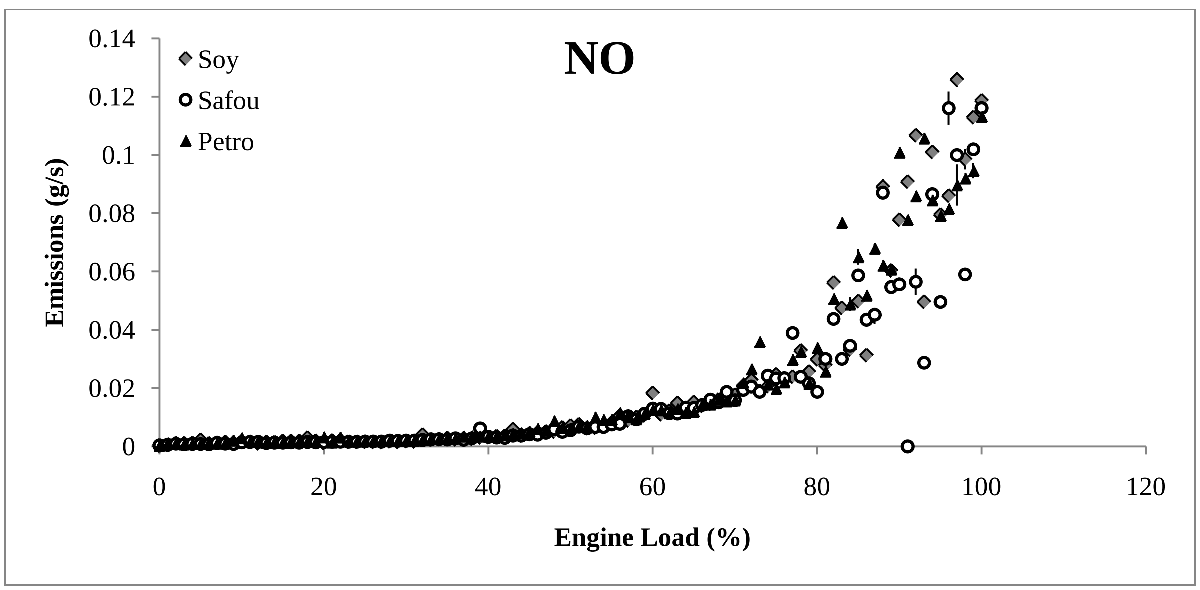


Figure 4.19. NO (g/s) emissions profile comparing Safou , soy, and petro.

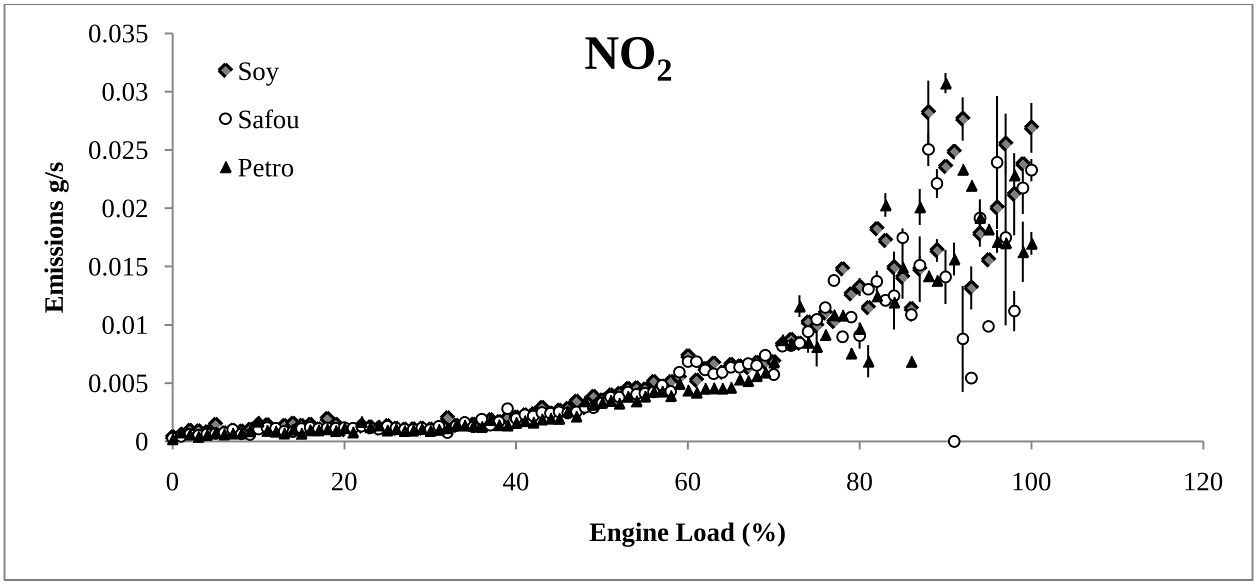


Figure 4.20. NO_2 (g/s) emissions profile comparing Safou , soy, and petro.

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CHAPTER 5

DISCUSSION AND CONCLUSIONS

Introduction

The primary objective of this work was to analyze Safou (*Dacryodes edulis*) in terms of the energy required to process its oil, and to characterize the biodiesel fuel potential of this oil feedstock. Energy analysis took into consideration process inputs and energy used in production. It also looked at the embodied energy of Safou oil and FAME produced, and investigated the potential of using production by-products such as seed and press-cake in terms of energy. Characterization of Safou FAME as a biodiesel included pre-combustion tests stipulated by ASTM 6571-09 and post-combustion measurement of emissions generated by the fuel.

Safou is still in its infancy as a domesticated crop for large-scale production of the fruit for food, yet alone for use as an oil crop. In light of the plant's oil production potential, this exploratory analysis of the oil as a biofuel feedstock, and analysis of the energy inputs required to create biodiesel from the fruit, was undertaken. In general, Safou has potential as a biofuel crop. Several points are made in this Chapter that help to identify the potential of the oil in terms of process and energy balance. More to the point, biodiesel production capacity from Safou appears to be favorable in terms of an energy balance, and the derived fuel appears to be comparable to soy biodiesel in terms of regulated emissions. A discussion of these and other findings is organized sequentially below according to the research questions posed at the outset of this work, followed by more general conclusions.

Research Questions

The following questions were posed by this research:

RQ1: How much energy is embodied in Safou pulp, raw Safou oil, residual press-cake, and Fatty Acid Methyl Esters (FAME) biodiesel generated from the oil?

RQ2: What are the characteristics of Safou oil extracted from fruit pulp that has spoiled and has become inedible?

RQ3: What are the fuel characteristics (including molecular composition, lubricity, flash point, cloud-point and gel-point) of biodiesel (FAME) made from Safou oil?

RQ4: What kind of emissions profile does FAME fuel derived from Safou generate when combusted in a 2006 Volkswagen Jetta TDI engine, and how does the profile compare to petro-diesel and soy biodiesel fuel run under similar conditions?

Research Question 1

Research question one addressed how much energy is embodied in Safou pulp, raw Safou oil, residual press-cake, and FAME biodiesel generated from the oil. The findings for this question are summarized in Table 5.1 (an expanded version of Table 4.5), with fruit-specific energy values. Energy density of oil and oil production byproducts were essential to informing several calculations that are pertinent to the following research questions. The use of the bomb calorimeter for this step is the most conventional method for determining energy density of a material.

Table 5.1
Summary of the Energy Content of Safou Oil, Press Cake, Seed, and Safou derived FAME

Sample	Energy	Unit
FAME	20.632	kJ/g
Oil	19.894	kJ/g
Press-Cake	15.175	kJ/g
Seed	11.587[a]	kJ/g
Average kJ /fruit		
Seed	82	kJ
Pulp	272	kJ
Total	352	kJ

[a] Value was not corrected for acid production but titration results were less than press-cake values and acid corrections of 0.9kJ/g.

Energy of harvesting. Although Safou production has increased in western Africa and crop developments such as marcotting allow for the propagation of plants with select traits, harvest efficiency remains unclear. Field data collected for this research was limited, but data collected for harvesting a tree considered on the large side for plantation applications showed that the collection of ~40kg of fruit in ~45 minutes by three people. Considering the tree's size and that the harvesters were neither trained nor working to maximize yield per labor hour, this number could be perceived as a minimal yield per time unit. It can also be assumed that production scenarios for Safou under optimal conditions in controlled plantation settings would yield considerably more fruit per labor hour. Given a similar plantation set-up as for oranges, an experienced harvester can fill six 40 kg boxes per hour and as many as nine in ideal conditions (Morton, 1987). Assuming an average 300 grams per orange, the total pick would be, at minimum, 800 fruit per hour. If he same fruit pick per hour picking safou would result in 50 kg per labor hour. Mechanization of crop harvest for oil production depends heavily on the end purpose of the fruit. If immediate processing for oil was planned then damage to fruit due to mechanized harvesting could be negligible. Furthermore, life on the tree could be extended, which has been demonstrated to be advantageous since oil content increases with fruit maturity.

Pulp processing and decorticating. Processing Safou fruit by hand for drying is a labor-intensive endeavor requiring, for this study, an hour of labor to process less than 4.5 kg of fruit. A mechanized or semi-mechanized system would be required to minimize this labor demand. Not only is the process used in this study prohibitive in terms of energy balance and production cost, but personal experience and feedback from individuals who helped with pulp processing for this study suggested that people would not be willing to undertake such a labor-intensive process. A method of slicing up fruit similar to a French fry press, or letting fruit spoil on purpose in order to separate the pulp in perforated tumblers, would need to be investigated. Water separation techniques could be employed to float fresh pulp away from seed clusters or to separate spoiled pulp from floating seed clusters.

Fruit pulp drying and pressing energy balance. The methods used for drying and pressing Safou pulp for oil proved to require more energy (21,834 kJ/kg) than was embodied in the oil (19,894 kJ/kg). Drying of fruit pulp proved to be the primary energy consumer with the methods employed for this research. However, when compared to cited energy demands for drying and pressing, the energy balance could prove to be favorable. The energy demands for a forced-air solar drier designed for operation in humid tropics were Safou is grown has been reported to require as little as 26Wh/kg (93.6 kJ/kg). Energy demand for screw presses has been reported to be as low as 36 Wh/kg of oil. The ratio of the sum of these two energy demands 62 Wh/kg (223.2 kJ/kg) compared to the energy density of Safou oil is 1:89, or just over 1%. Although these estimates do not include actual, measured energy demand and losses during processing, they do illustrate that it may be possible to achieve a significantly more favorable energy ratio in comparison to the energy balance resulting from methods used during this research.

Process energy from seeds or press-cake.

Seeds. The energy in dried seeds is sufficient to process the fruit's needs for drying and pressing pulp. Seed content of wet fruit is less than 25% based on wet weight. A dry weight comparison per fruit oil yield shows that each fruit can produce approximately 9.6 g of neat oil, assuming yields of 47% (dry weight). This would require 4.6 kJ of process energy per fruit (9.6 g x 0.223 kJ/g = 2.14 kJ). If the seed content is 25% by weight and 10% of that is moisture, then on average each fruit would have 13.77 grams of dried seed or, in terms of energy, 151 kJ of energy per fruit. If we were to assume that drying and pressing required for oil production does only require 0.223 kJ/g, then the seed content of Safou fruit could be used to provide the necessary energy. Seeds have a conservative energy content of 11 kJ/g and could provide sufficient energy for processing even if the heat and power conversion efficiency was as low as 4%. Tests for general combustion gasification of the seeds would be necessary to confirm the possibility of this energy conversion for further development. Moisture content of seeds in this study was found to be less than 20%, which is the upper limit for consistent combustion of biomass materials.

Press-cake. Embodied energy content of press-cake was determined to be greater than 15 kJ/g. As in the case of seeds, the energy content of this material could be applied for process energy. However, the potential for press-cake to be used as a food additive may be financially more viable than direct energy conversion, but in the case of spoiled pulp, food applications may not be possible.

Press energy example. If a press was run with Safou biodiesel, how much oil could be produced? Assuming a conservative estimate that the press energy demand was 100 Wh/kg of oil produced, one liter of Safou biodiesel could produce 14.66 kg of Safou oil. This number was arrived at by calculating the energy content of Safou biodiesel and its application in a diesel engine driving a press. See equations 1-4 for a summary of the calculations.

(1)

(2)

(3)

(4)

Research Question 2

Answering this question required investigation of the spoiled fruit pulp and its oil potential. The question specifically inquired as to the characteristics of Safou oil extracted from fruit pulp that has spoiled and is inedible. Spoiled fruit pulp appears to be salvageable, if not for human consumption, then at least for applications in cosmetics and biofuels.

Several GC/MS results were produced regarding the fuel produced from spoiled fruit, and its chemical composition was similar to that of the test fuel made from unspoiled fruit. Figures 5.3-5.4 provide an overview of the comparison between the test fuels made from ripe and from spoiled Safou derived FAME that was tested.

Reclaiming post-harvest losses. Safou has enjoyed almost two decades of intentional inquiry into the crop's potential for agroforestry systems in tropical regions where it is indigenous. The crop's oil potential is simply one of its many characteristics that recommend it for incorporation into farming systems in tropical western Africa. Developments in the crop's propagation to maximize yields and ease of fruit production have considerable implications for agricultural livelihoods. The fruit crop's limitations in terms of shelf life and the estimated 40-50% post harvest-losses still remain a problem in spite of some discoveries that have helped to minimize losses. As identified by this research, spoiled fruit can be reclaimed for the production of oil. The titration level of 3.01 g^{KOH} per liter identified in Table 4.4 is acceptable for biodiesel feedstock. At what point the spoilage is detrimental to oil reclamation or limits its uses is undetermined. Nevertheless, oil that may not be salvageable for food purposes may retain its potential for fuel and cosmetic applications. As can be seen by comparing Figure 5.1 to Figure 5.2, the spoiled Safou pulp FAME is similar to the Safou test fuel, suggesting that the two are comparable as fuels.

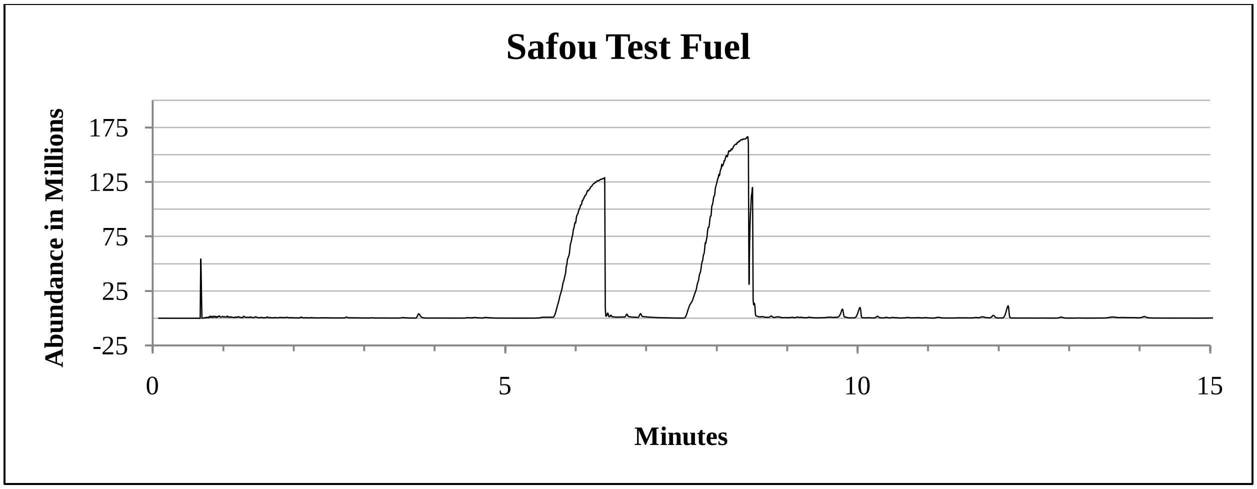

Figure 5.1. GC of Safou test fuel.

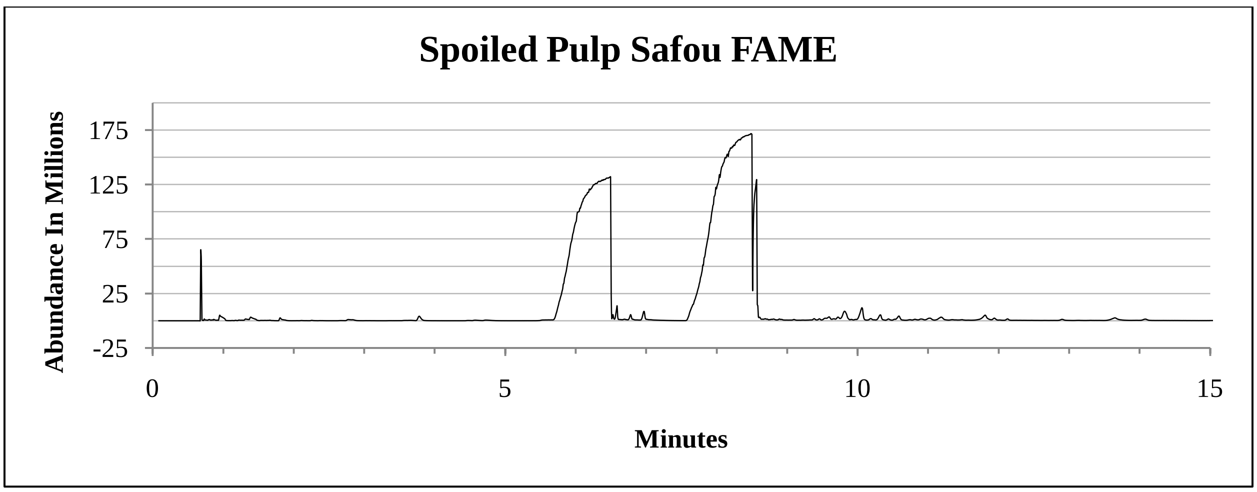

Figure 5.2. GC of spoiled pulp Safou FAME.

Research Question 3

This question required an investigation into the pre-combustion characteristics of the Safou fuel. 200 ml of test fuel was given to Jeremy Ferrell, Outreach and Production Manager for the Appalachian Biodiesel Research and Testing Facility, who was kind enough to run several ASTM-pertinent tests. Safou test fuel did not pass all of the stringent ASTM specifications, but the tests that were performed provide a foundation for the oil's potential as a fuel. While failure to pass may be due to characteristics inherent to the feedstock, complicating reactions due to human error during and after production were more likely the culprit. Test batches that were successful using stir plates and glassware were not as successful when attempted at the five-gallon level. Although reaction ingredients and molar ratios were maintained, the reaction vessel, method of agitation, and temperature were not consistent and are suspected to have affected the reaction. Considerable fuel polishing was performed, but these processes are hindered when incomplete or contaminated reactions occur prior to polishing. ASTM tests revealed that triglycerides were present, indicative of post-reaction contamination because mono- and di-glycerides were absent.   In spite of failing to pass the strict ASTM standards for biodiesel the grade of fuel produced would likely be representative of fuel produced in developing nations where Safou is grown. Because of the fuel's cloud point of 55° F it would recommended primarily for use in tropical regions where the fruit is grown. Figures 5.1 through 5.4 are results from GC tests done on the various test fuels as well as on the spoiled fruit pulp fuel. These figures show that petro diesel has a much larger concentration of molecules with lower individual molecular weights in comparison to the biodiesels. Soy has a lower concentration of the C:16 molecule compared to Safou, as shown by the area under the peak above the six-minute mark. Furthermore, the spoiled Safou FAME appears to be comparable to the Safou test fuel, suggesting that spoiled Safou pulp oil is relatively similar to the unspoiled Safou pulp oil that was converted to fuel.

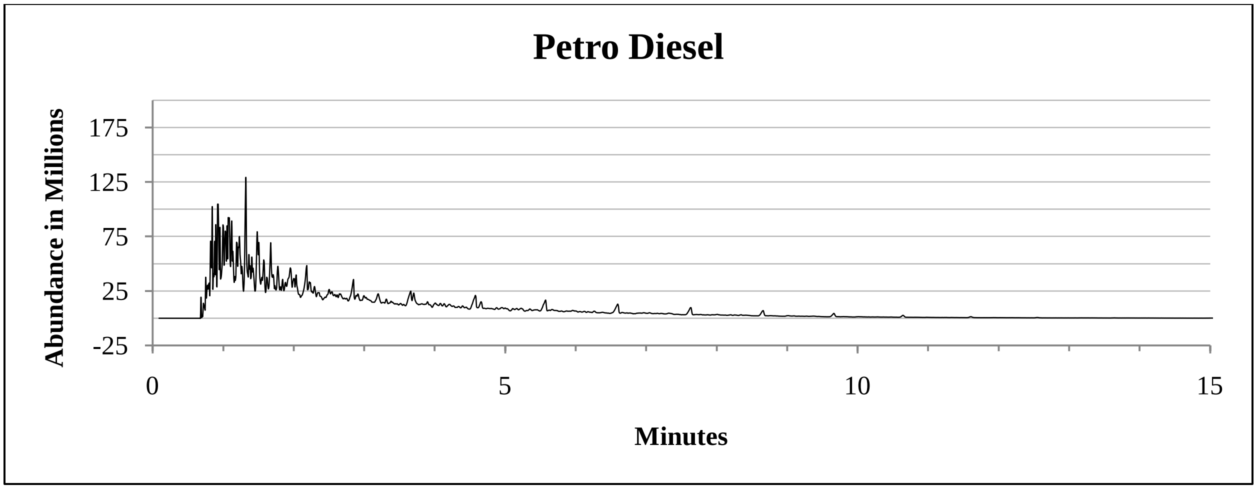

Figure 5.3. GC of petro test fuel.

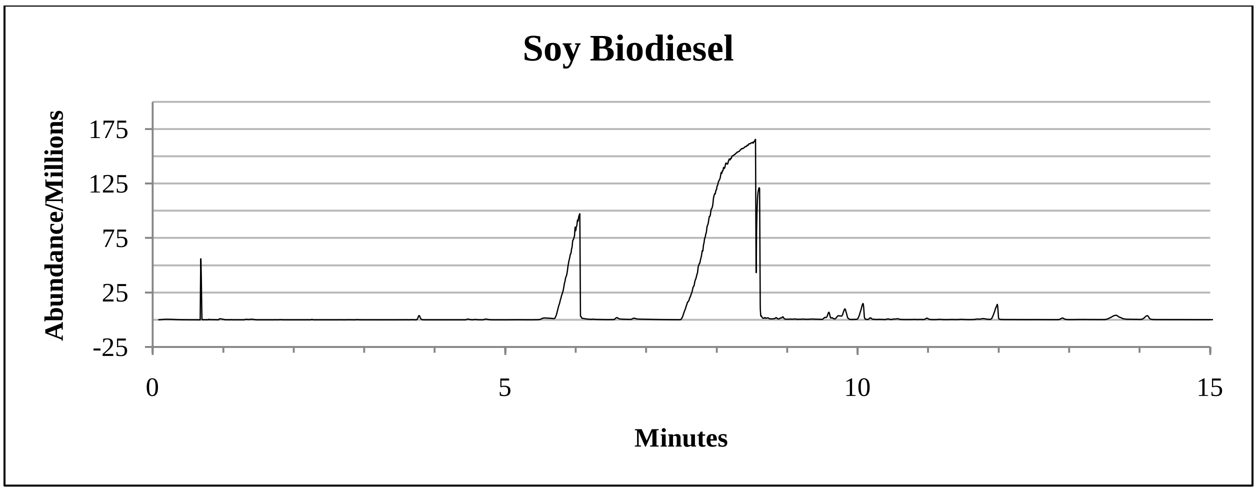

Figure 5.4. GC of soy test fuel.

Research Question 4

This question asked what kind of emissions profile Safou fuel generates when combusted in a 2006 Volkswagen Jetta TDI engine, and how that profile compares to petro-diesel and soy biodiesel fuel run under similar conditions. The comparison of the emissions between the various test fuels was hindered by the absence of exhaust flow meter (EFM) data. Flow was back-calculated using several other engine parameters and data specific to the rate of fuel. To verify this strategy, comparisons were performed on previous emissions data sets that included EFM data and that had comparable testing conditions. This comparison shows an acceptable distribution. Although the emissions values are not absolute, they proved to be sufficient for a comparative analysis of Safou in relation to soy and petro diesel. Initial findings indicate that, overall, Safou performs at a level equivalent to soy and petro diesel. There are instances where Safou appears to perform somewhat better or worse than soy or petro diesel; however, Safou is not uniquely superior or inferior in a comprehensive comparison. Further discussion is provided below.

Method of calculating emissions flow. Emission data collected for Safou, soy, and petro was collected for comparison. Unfortunately, the exhaust flow data was not measured and a flow calculation was required in order to compare the emissions. The calculation summarized below was applied to each data point, which was binned every second. This calculation compared total mass of emissions over time. Equation 5 summarizes the primary units required for the equation, while Equation 6 includes constant values and the variables for RPM, kPa, and Temperature. Initial computation is in grams per second and then converted to kg/hr.

(5)

Ve = Volumetric efficiency of the engine
Ed = Engine displacement in cc
Pressure = Manifold pressure
Temp (K)= Engine intake temperature, which is hotter than ambient.

(6)

In order to validate this method a comparison of measured data (including EFM values) and calculated data for petro and soy was done. A percent difference was generated using Equation 7.

(7)

A histogram was then generated for each fuel, as shown in Figures 5.5 and 5.6. The primary concentration of values was between -50 and zero, and the charts focused on this segment. As can be seen in Figure 5.5, the distribution of petro is left of zero with a primary peak centered around -7. Figure 5.6 shows soy and the distribution is asymmetrical with a peak right at zero and a secondary peek well left of zero centered at -33. At first this comparison appears to be significantly different; however, when the averages of the bins are compared there is a curious similarity. The average bin value of petro is 19, while the average value of soy is 18. As varied as the distributions first appear, the fact that the averages of each fuel are approximately 5% different when compared. This implies a fundamental similarity despite the different histogram profiles. When the averages of the difference were calculated prior to rounding, soy had an average of -39.31 while petro had an average of -38.57. When comparing one fuel to the other this is a percent difference of less than one. The implication of this comparison is that while the distribution is not alike for both fuels, a comparison between fuels with the calculated data has some merit.

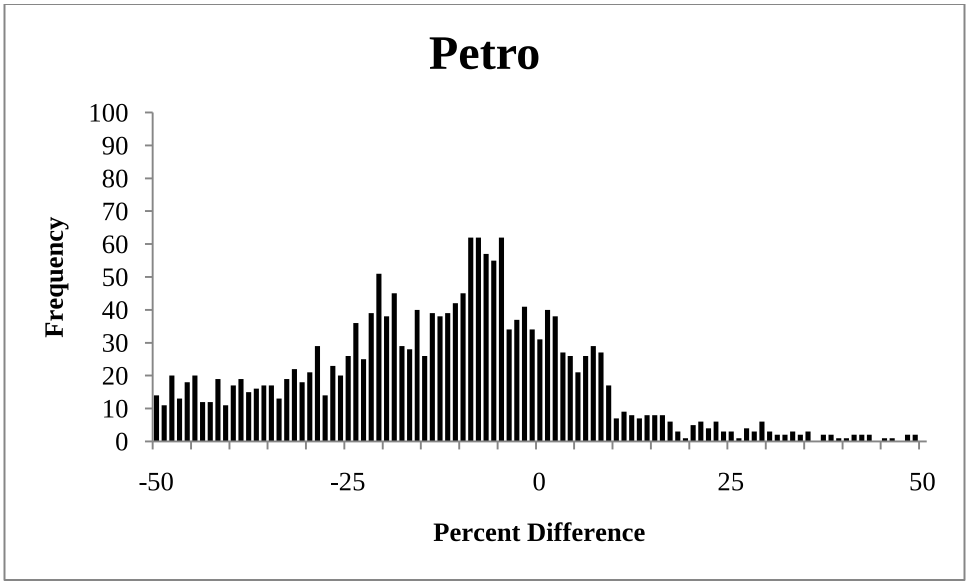

Figure 5.5. Percent difference of measured vs. calculated mass flow data for petro.

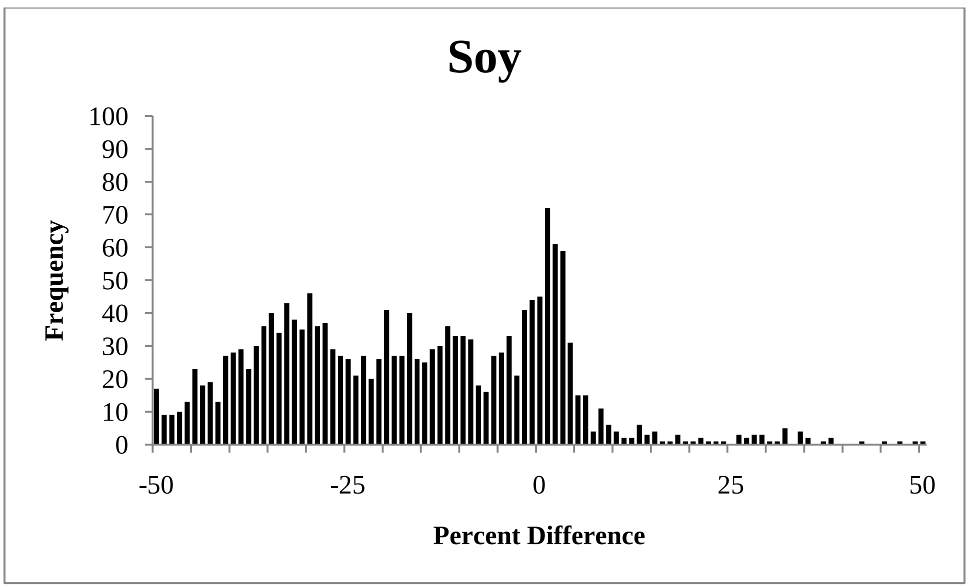

Figure 5.6. Percent difference of measured vs. calculated mass flow data for soy.

Safou test fuel. The Safou FAME produced for emissions testing was assessed for its compliance to ASTM standards for biodiesel. The Safou fuel could not be termed Safou biodiesel in the strictest sense because it did not meet all the criteria in order to be certified. Therefore, for the purposes of this research, Safou fuel was labeled "Test Fuel." ASTM results as indicated in Table 4.7 were indicative of incomplete reaction and/or contamination of the sample with raw oil.

Emissions data. Emission data was graphed against engine load because engine load appears to be directly or indirectly correlated with many variables that affect emissions. For purposes of comparison, in this section emissions were converted to g/mi by including speed for each data point. The basic equation is shown in Equation 8.

(8)

General emissions overview. In all cases there was little statistically significant variability between fuels at engine loads below 30%. Error for this range was statistically insignificant. Error bars are represented by the vertical lines in the graphs. Data points above 80% engine load were limited so error was not minimized so comparisons for this range are limited, however there does seem to be some suggested trends that would require further testing and a more robust data set in order to do any meaningful comparison. The range between 30% engine load and 80% has a sufficient data set with variation and statistically insignificant error. The following comparisons are based on grams per mile and focus primarily on the 30-80% engine load range.

Comparison of CO_2 between fuels. Figure 5.7 shows CO_2 for all three fuels. As can be seen, the fuels are comparable at engine loads 20% and below. Variation between fuels begins around 30% engine load, most likely due to gear shifting and RPM variations. No single fuel appears to outperform any other fuel; however, within the range of 30-80% engine load data for Safou is more consistently the lowest value or shares the lowest value 34 of 50 times, compared to petro's 20 out of 50 data points or soy's 11 of 50 points. Sharing a lowest point was determined by overlap of points or their error bars. This would suggest that Safou produces less CO_2 in this engine load range than do the other fuels.

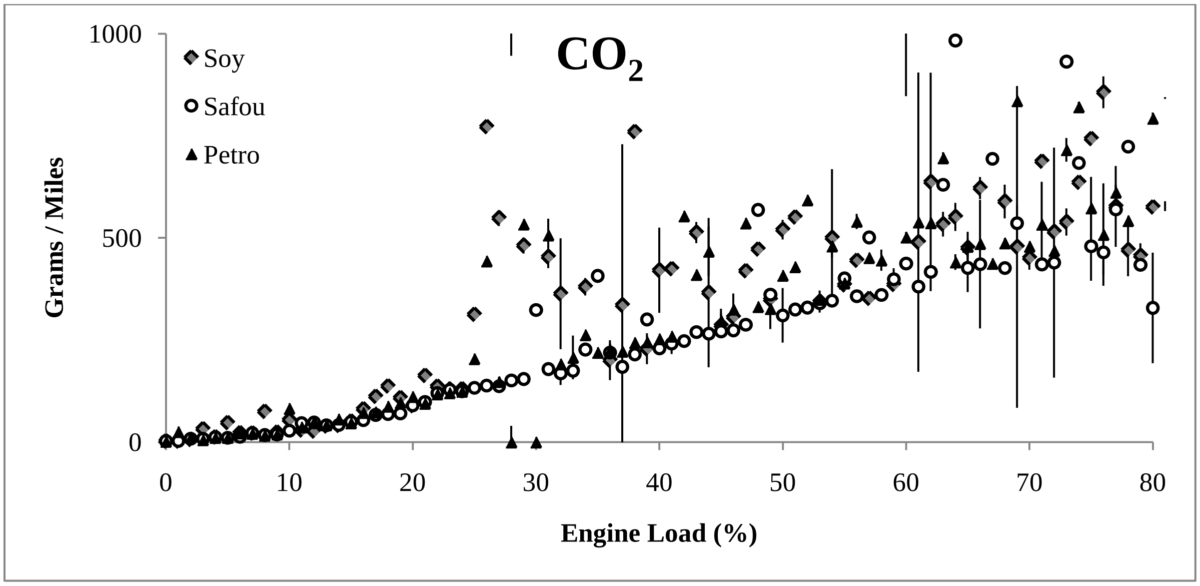

Figure 5.7. CO_2 g/mi emissions for Safou, soy, and petro over 0-80% engine loads

Comparison of CO between fuels. A comparison of CO across fuels shows that petro diesel uniquely holds or shares the lowest value of 68 of the 80 data points, excluding the two zero values for petro at engine loads 29 and 31. Soy shares six lowest values, while Safou shares or holds 19 lowest values.

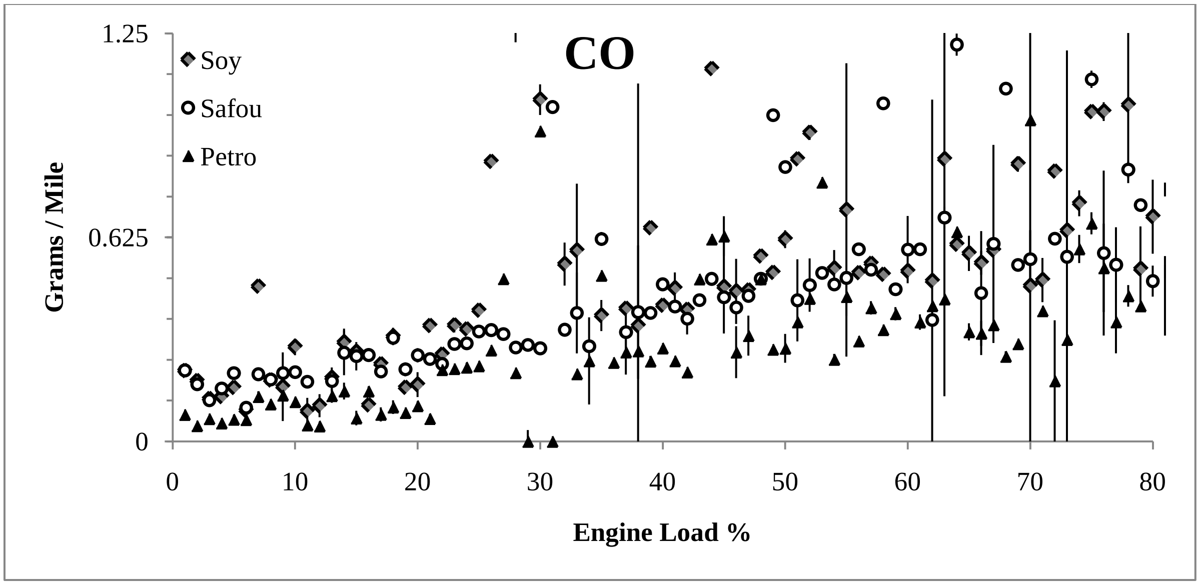

Figure 5.8. CO g/mi emissions for Safou, soy, and petro over 0-80% engine loads.

Comparison of THC between fuels. Total hydrocarbons are indicative of incomplete combustion both in the cylinder and in the catalytic converter. During increased engine load the engine is injecting more fuel than can be completely combusted. As RPM increases for a given gear ratio, latency of fuel in the cylinder decreases, resulting in incomplete combustion. At upshift, latency increases for the increased fuel mass, decreasing THC production. When increased work is needed at higher percent engine load and shifting up would stall the engine, RPMs are increased again, decreasing latency of fuel in the combustion conditions and producing more THC. This explains the general undulation of the THC data as engine load increases (Figure 5.9). However, THC count is also affected by the catalytic converter. Due to the surface area and the proximity of the various gases going through the catalytic converter, catalytic efficiency increases with increased saturation of target gases, up to a point. This may be due to molecular proximity of gases to catalytic elements being reduced. Increased saturation of gases is also correlated to increased flow, which reduces overall latency in the converter, decreasing conversion of target gases.

Consequently, it would be expected that as THC increases in emissions then target gases such as CO_2 would decrease. Pre-converter emissions may be leveled out in comparison between gases. System design injects additional fuel into certain cylinders in order to increase hydrocarbon count without changing engine speed. This excess fuel or hydrocarbons are intended to saturate the catalytic converter in order to drive the catalytic process, producing more CO_2, NO_2, and water.

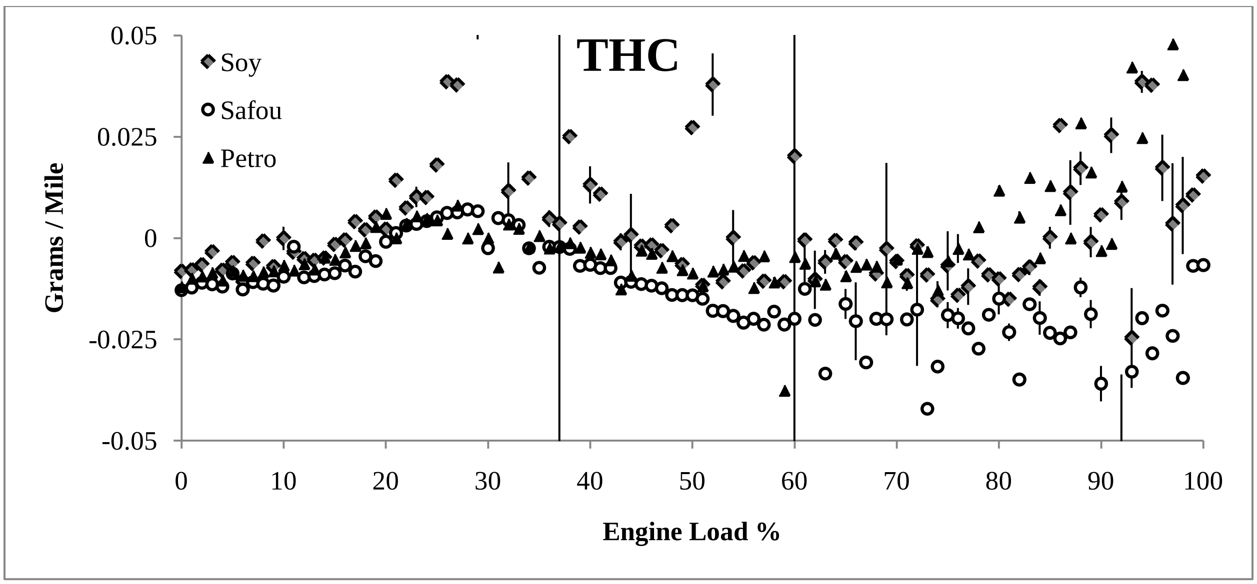

Figure 5.9. CO g/mi emissions for Safou, soy, and petro over 0-80% engine loads.

It is curious that the 40-60% engine load area shows petroleum increasing in THC values in comparison to Safou, while the CO comparison shows petro with the least production of CO. This points to the fact that the catalytic converter is designed to be more efficient with the range of hydrocarbons in petro diesel fuel. Safou may perform better in terms of THC because the carbon chains present in the fuel are larger than those present in petro and soy, but this may not be ideal for catalytic design. Although there was potential drift in the THC readings, the fact that Safou was recorded between both fuels does suggest a notable difference, but would require further investigation to confirm why there is a difference.

Comparison of NO between fuels. NO production for all three fuels appears to be very similar up to 25% engine load, at which point emissions data begin to stratify with the greatest variation in readings for soy. Safou appears to compare closely to petroleum. If the THC values reported above are accurate there appears to be a correlation between lower THC and lower NO production, suggesting a potential conversion correlation between Safou THC and NO reduction. Looking at the 40-60% load range for NO, Safou appears to most consistently have the lowest values. Compared to the same engine load range for THC there appears to be a potential correlation.

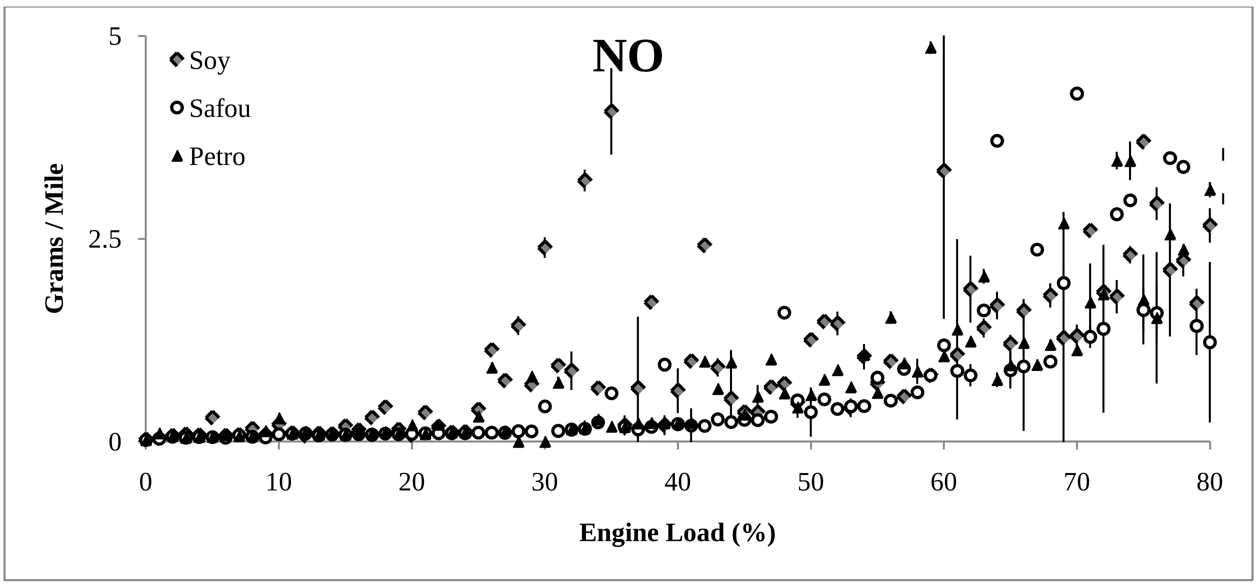

Figure 5.10. NO g/mi emissions for Safou, soy and petro over 0-80% engine loads.

Comparison of NO_2 between fuels. Generally, NO_2 production for the three test fuels is similar. The trend for petroleum appears to gravitate towards the lower values, with increased separation of the data points as engine load increases. There is a suggestion of stratification or notable increase for soy and Safou between 38-50% engine load and again at 60-70% engine load. When this is compared to the NO data in Figure 5.9, Safou values appear to be generally lower than petro. This disparity may be due to several reasons. Safou may initially produce more NO_2 during combustion, or it may experience increased efficiency of the catalytic converter in this range. More likely it is a combination of the two. The upshot is that across engine loads NO_2 production is at times comparable while at other times varyies sufficiently to be notable.

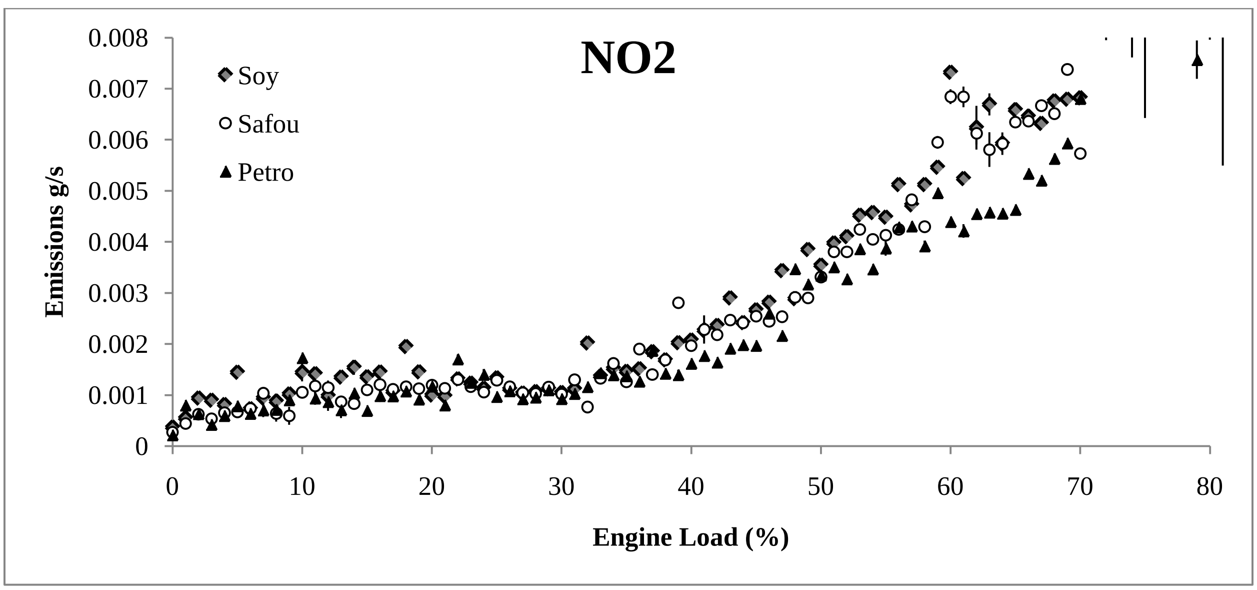

Figure 5.11. NO_2 g/mi emissions for Safou, soy and petro over 0-80% engine loads.

General Discussion

Emissions. It appears that Safou emissions are comparable to other fuels such as soy and petroleum diesel. These results show the Safou test fuel was not necessarily better or worse compared to soy and petro, but there appear to be variations during certain operating conditions, including at different engine loads. The data set compiled for this research appears to be sufficiently robust to suggest that, although there are differences in emissions between Safou biodiesel and petro, Safou is not decidedly better or necessarily worse than petro diesel in terms of controlled emissions production. It does, however, suggest different system responses at particular points of operation. The broader implication is that biodiesel fuel in general is being evaluated under a system that is designed to optimize emissions reductions for petroleum diesel.

Engine design and emissions. The Jetta TDI Engine system is designed to use petroleum diesel. Although some emissions may be affected by passive system design (e.g., the catalytic converter), other effects may be due to active system responses such as variation in injection timing and in when the emissions gas return valve is open. The impetus to change the underlying system design of the engine to accommodate biodiesel is lacking because the fuel is closely comparable to petroleum diesel and the market demand is primarily for blending biodiesel with petro diesel. However, if biodiesel use becomes more prominent—as has been the case with ethanol, which has promoted flex fuel design—diesel engine systems in light-duty vehicles may become akin to flex-diesel and able to accommodate fuel differences by modifying combustion variables such as injection timing, air-fuel ratio, and temperature.

Safou as biofuel. According to the findings of this research, Safou has potential as a biofuel feedstock. Although the scope of the energy balance assessment is limited, the potential energy balance is favorable if strategies such as providing energy from seed were adopted. The prospect of reclaiming post-harvest losses via oil extraction for fuel by using fruit too spoiled for food use is possible. This strategy is also potentially favorable in terms of energy balance because of the greater ease in separating the pulp. Emissions generated by Safou are not uniquely better or worse than those of petro diesel or biodiesel despite some variation in emissions performance. Although the Safou industry is in its infancy, the potential to develop it further by providing necessary energy for food production is a possibility. Obstacles to Safou being used as an oil crop are being investigated and over the last decade substantial progress has been made. It is possible that in the coming years the Safou industry could expand and fuel its own expansion.

Suggestions for Further Research

Safou Biodiesel

This research has established that Safou has potential as a biofuel in terms of energy balance as well emissions profile. The limited data set would need to be further expanded in order to establish the fuel's strengths and weaknesses and under what operating conditions. It would be ideal to produce ASTM-certified Safou biodiesel and compare the fuel to petroleum derived diesel as well as biodiesels from a variety of feedstocks.

Catalytic Converter Design

The catalytic converter may have varying effects on the final emissions of a fuel. It would be very informative to compare pre-catalytic and post-catalytic emissions. The implications for passive catalytic design or active system responses such as EGR and rich combustion conditions meant to fuel the catalytic process should be explored specifically for biodiesel.

Spoiled Safou Fruit

The potential to reclaim post-harvest losses due to fruit spoilage should be further explored. The point at which oil extraction from spoiled pulp is optimal needs to be investigated further and placed in the larger context of competing needs from the food, cosmetics, and fuel industries.

Energy Conversion of Safou Seed and Press-cake

Determining whether seed or press-cake can be used to provide the energy for processing needs further investigation. Despite the fact that the energy required for processing is available in the seeds and press-cake, avenues of converting this energy need to be further investigated. Thermal decomposition such as direct combustion or gasification should also be investigated.

Safou and Anaerobic Digestion

While thermal conversion of seed and press-cake may be possible, the option of anaerobic digestion of the seed, press-cake, and even the pulp should be investigated. The potential to feed anaerobic digesters with spoiled fruit for biogas production should also be investigated. Residual effluent of Safou biogas production could have further potential as a crop fertilizer, but this is presently unproven.

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BIOGRAPHICAL INFROMATION

Daniel Allen Law was born December 1, 1978 at Tshikaji Hospital just outside of the rail town of Kananga. At that time the country was called Zaire; more recently it has been renamed the Democratic Republic of Congo (DRC). The son of David and Leveda Law, Daniel spent much of his young life in and around agricultural and medical development projects in the DRC.

Law went to high school in Kenay, attending Rift Valley Academy and graduating in 1997. He then went on to earn his BA with a double major in Ceramic Arts and French Poetry in 2002 from Asbury College (now Asbury University) in Kentucky (USA). His experience in the DRC led him to return to teach at The American School of Kinshasa (TASOK) from 2002-2004 and later to build a wood-fired kiln at the Academie des Beaux Arts with the Mennonite Central Committee (MCC-Congo) in 2005.

In 2006, Law married Molly Lane who he had met in the DRC during his tenure at TASOK. After the birth of their daughter Sophia they moved to Boone, North Carolina so that Daniel could pursue a Master of Science degree in Appropriate Technology at Appalachian State University, as part of which this work was produced. During the second year of Daniel's program their son Xander was born.

Having earned his Master of Science in Technology in December 2010, Daniel will be working on biofuels emissions testing in the short term. In the longer term Daniel plans to work in the developing regions of the world on agriculturally-based appropriate technology initiatives, ideally focusing in on biofuels and value-added processing.