ATTALEA PHALERATA AND BIODIESEL: IMPLICATIONS FOR LOCAL AND REGIONAL SUSTAINABILITY

A THESIS SUBMITTED TO THE GLOBAL ENVIRONMENTAL SCIENCE UNDERGRADUATE DIVISION IN PARTIAL FULFILLMENT OF REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

GLOBAL ENVIRONMENTAL SCIENCE

MAY 2005

By
Graceson Ghen

Thesis Advisor
Fred T. Mackenzie

TABLE OF CONTENTS

Acknowlegements

First and foremost a hugemangous Mahalo must go out to Fred Mackenzie, Jane Schoonmaker and the financial support of NOAA without whom I would never have been able to undertake this project. I would like to thank Foster Brown for getting me involved in this project. Also I would like to thank Anelise Regiani and Evandro Ferreira for including me in the project, answering questions, and supplying me with botanical information. A special thanks must go to Rui Santana de Menezes, Director of Unidade de Tecnologia de Alimentos (UTAL), who made my work in Acre really happen. Finally many thanks to fellow my students Mel, Johsons, Ervane, Rosangela, and everyone else at UTAL who helped me in so many ways.

Abstract

As biodiesel grows in importance as an alternative fuel it is important to consider the implications that its large scale production and combustion have on biogeochemistry and the environment both globally and regionally. With this in mind the lifecycles of petroleum diesel and biodiesel are discussed in relation to influences on a few key biogeochemical cycles. While biodiesel is likely to have less impact than petroleum diesel on biogeochemical cycles due to combustion, the overall lifecycle for biodiesel production requires significantly larger quantities of water and nutrients. For a region considering large scale production of oil crops, increases in water and fertilizer consumption are important considerations for sustainability.

Rural communities of the Amazon Basin depend greatly on forest resources. In the Brazilian State of Acre where oil prices are high, these communities can benefit from the development of alternative fuel sources like biodiesel. This region of the Amazon has many species of plants that produce high quantities of oil in their fruits and/or seeds. Initial production estimates and physio-chemical analysis for one potential species, the palm *Attalea phalerata*, are presented. Field observations and collections were used for per tree production estimates. Basic nutritional analysis of the fruit and kernel included protein, fiber, ash, humidity, and lipid content. Oil was extracted for analysis using petroleum ethanol solvent from the fruit and kernel. Analysis of these oils included saponification, acid, iodine, and peroxide indexes. Results indicate that the fruit and kernel contain approximately 20 and 70 percent oil, respectively. *Attalea phalerata* proves to be a promising species for diversified, small scale, communities working

towards sustainability providing a range of useful products including oil, food for humans and animals, building materials and charcoal.

LIST OF TABLES

LIST OF FIGURES

Chapter I

INRODUCTION

The limited nature of Earth's natural resources has become increasingly obvious during the last several decades. The use of combustible fuels, such as petroleum, is among the most apparent and immediately pressing natural resource issues facing human societies. Nearly the entire human population of the planet is directly dependent on fossil fuels, coal, oil and gas, for use in energy production and transportation of people and goods. With the peak of global oil extraction predicted to be early in this century (Deffeyes, 2001), we can expect to see steady increases in petroleum costs and a surge in the use of renewable energy sources such as solar, wind, hydroelectric, and biofuels.

Biofuel is a general term used for fuels that are basically biological in origin and include materials like wood, and vegetable or animal fat. The use of biofuels is not a new idea; in fact biofuels have played an important role in the growth of civilizations since the first prehistoric human discovered fire. One may thus be inclined to think that biofuels are rudimentary in nature, and are not applicable in today's technologically advanced world. However this is not the case. In reality, since the industrial revolution, biofuels have simply been substituted by fossil fuels which are easily obtainable in vast amounts, and are not dependent upon seasonal and climatic conditions.

The substitution of petroleum fuel for biofuel is perhaps best demonstrated by the diesel engine, an engine synonymous with petroleum and vital to every transport industry in the world. The first diesel engine developed in 1895 by Dr. Rudolf Diesel was designed to run on a variety of fuels, including vegetable oils. Rudolf Diesel believed that his engine could be used by farmers to increase productivity while growing their own

fuel. Such a system would provide strong internal economic stimulation to any country that practiced agriculture. However, petroleum could also be used in the diesel engine and given the price and quantities of petroleum worldwide at this time, it is not surprising that vegetable oil was quickly "forgotten" as a viable fuel source. The design of the original diesel engine was then altered to run on a cheaper less viscous fuel, a byproduct of gasoline distillation, that the petroleum industry named "diesel fuel".

Today, due to issues ranging from global climate change to predicted decreases in petroleum production, biofuels and other alternative energy sources are becoming increasingly popular. Perhaps the most deciding factor influencing the adoption of alternative energies is the cost of converting a system using fossil fuels into one that can run on an alternative fuel. In general it can be said that the easier and cheaper the conversion, the faster it will be adopted. It is not surprising then that the use of "Biodiesel" as a substitute for petroleum diesel in the modern diesel engine has been growing very rapidly.

In many regions of the world, the use of biodiesel is simply an attempt to supplement petroleum diesel in response to rising petroleum costs, while in other areas biodiesel use is a conscious effort to use alternative and sustainable fuels. In some regions recycled cooking oil is used, while in others entire oil crops are consumed for biodiesel production.

A major focus of this work is the exploration of the feasibility of biodiesel production and consumption on a large scale. Chapter 5 examines the details of biodiesel, and compares of the "lifecycles" of petroleum diesel and biodiesel in relation to production, combustion and influences on biogeochemical cycling. Although it is highly

unlikely that biodiesel could ever be a substitute for petroleum in the quantities consumed worldwide, it may prove to be a viable fuel source for small regions using a sustainable approach to energy production. In areas such as the Amazon Basin of South America, hundreds of native plant species capable of producing large quantities of oil exist, but remain underutilized.

The research work presented in this paper deals with the potential of one such species as a source for biodiesel production for rural communities of the Southwest Amazon. *Attalea phalerata*, or uricuri, is a palm that is common throughout the Southwestern Amazon. Chapter 2 examines *A. phalerata*; its the botanical characteristics, geographic distribution, cultural uses. In Chapter 3 and 4 the nutritional and physiochemical properties of the fruit and oils are discussed. This research was conducted as part of a larger research project entitled "Potencial de Produção de Biodiesel no Vale do Acre" (Potential for Production of Biodiesel in the Acre Plain), which is focused on the potential of ten selected oil rich species to be used as a sustainable fuel source for rural communities of the Southwest Amazon region. The research was conducted in the Brazilian State of Acre, at the Federal University of Acre's (UFAC) Unit of Food Technology (UTAL) facilities in Rio Branco.

In the context of large scale production, I conclude that *A. phalerata* is a specie that has significant oil producing potential, although the difficulties associated with processing and oil extraction do hinder any immediate large scale ventures. However, given the numerous uses and abundance of this species, I also conclude that *A. phalerata* is a forest resource that has definite potential to be part of a sustainable development approach, especially for isolated rural communities, providing a range of useful products

including oil (for consumption and biodiesel production), charcoal, food, and building materials.

Chapter II

ATTALEA PHALERATA: Botanical Description and Cultural Uses

Attalea phalerata (Figure 2.1) is a palm found in the Amazon Forest of Columbia, Peru, Bolivia, and the states of Acre, Mato Grosso, Pará and Tocantins in Brazil. In Brazil *A. phalerata* is commonly called Uricuri, or Urucuri, and in Bolivia it is known as Mocatú. *A. phalerata* grows at altitudes up to 1,000 m, in dry regions with low elevation, in open areas, riverside forests, and in the forests of the Amazon Plain. In Acre it is found in large numbers in perturbed forest areas, especially pasturelands where it establishes itself very easily. In the lands around Rio Branco, Acre, the area where this study was conducted, *A. phalerata* is the most commonly occurring palm species.

Attalea phalerata shares many of the same uses and is very similar to *Attalea speciosa, or Babaçu,* a palm very common in the states of Maranhão and Tocantins. Here, Babaçu occurs in vast numbers, and plays a very important role in the lives of the people of this region. For many, Babaçu palms are a crucial source of food, fuel, shelter and income. The fruits provide food from the mesocarp and oil from the kernel. The dried and burnt shells of the fruit are used by many families to make a high quality charcoal, and the leaves are utilized for thatching, baskets, fans, and many other items. Production of Babaçcu kernel oil has become a significant industry in these states, with many family incomes solely dependent upon the harvesting and processing of fruits from naturally occurring stands. While the fruits of *A. phalerata* are a bit smaller than those of *A. speciosa,* the kernel makes up a larger percentage of the fruit, and is generally easier to harvest given the shorter height of the *A. phalerata* palms.

Figure 2.1: Mature *A. phalerata* palm with two fruit stalks, Rio Branco Acre.

Botanical Description

Trunk: solitary, 2-8 m in length, 20-35 cm in diameter, sometimes completely covered with persistent dead leaves. LEAVES: 12-20*;* Leaf sheath 0.5-1.7 m in length with fine fibers along the edges; Petiole 40-69 cm in length; Rachis 4.5-6.2 m in length; 106-199 pinnae per side, arranged regularly or irregularly in groups of 2-5, ordered along one or various planes, linear, aristate on the apices, Middle Pinnae with 88.5 cm of length, 4 cm in width, with or without auricle at the base and prominent central rib. Inflorescence: intrafoliar; Peduncle 50-70 cm in length; Peduncular bract 1.2 m in length, strongly externally furrowed; Rachis 40.5 cm in length, sometimes the pistilate rachis

appears swollen; 348 staminate rachillae 4-8 cm in length, arranged all around the rachis. Flowers: staminate 7 mm in length, arranged on just three sides of the rachillae, 3 sepals deltate, 3 free petals, linear, 6 stamates, pistiloide absent; pistilate flowers 2-6 per rachillae, arranged on just one side of the rachillae, 3 deltate sepals, 3 petals, staminoidal ring present. Fruit: densely arranged on the inflorescence; 8-11cm in length and 3.5-5cm in diamenter; form ellipsoid oblong; epicarp fiberous, fine, light brown in color; mesocarp meaty, oily, yellow color, sometimes almost orange; endocarp with distinctively grouped fibers. Kernels: 1-4 per fruit.

Cultural Uses and Economic Importance

Fruit:

Figure 2.2: Three *A. phalerata* fruit, showing typical variation in size.

The fruits shown in Figure 2.2 are very well known in Acre and are commonly referred to as “coquinho”. They are consumed raw and sold in the markets of Rio Branco

in bags of about 10 fruits for about US$ 0.25 during harvest time and about US$ 0.50 between harvest times (Ferreira, 2004). An average stalk of about 300 fruits would thus cost between US $7.50 to $15.00. Because *A. phalerata* is so common, almost the entire harvest of the fruit originates from naturally occurring stands. The collectors are generally small agriculturists that come periodically to town, selling part of the harvest directly to the consumer and the remainder to other vendors**.**

Preferred fruits have an orange/yellow pulp, with minimal fibers, and a slightly sweet flavor. To know if the fruits are ripe, one can use two strategies: check if the sepal-petal ("cap") at the base of the fruit can be removed easily, or if the husk is easily separated from the pulp from the base to the tip of the fruit. The most commonly applied technique used when eating the fruit is to bite the husk at the top of the fruit and peel it down to the base.

The fruits can be found practically all year round, indicating that there is a significantly long harvest period. Indeed, although the peak harvest season had passed at the time this research was conducted in June and July, 2004, there was no problem locating many palms in various stages of development from flowering to dropping ripe fruits.

Significant variations exist between the fruits from different *A. phalerata* palms. This can easily be seen in Figure 2.3**.** In this figure ten different fruit stalks all at the point of harvest are shown; variations exist between the number of fruits per stalk, the size and shape of the fruits, as well as the thickness, color, and quantity of the mesocarp and fibers within the mesocarp. This demonstrates that *A. phalerata*, as with many species of *Attalea*, has many morphological variations.

Figure 2.3: Ten mature *A. phalerata* fruit stalks used in this study.

Besides having a commercial value, *A. phalerata* has importance in rural populations. Among the Seringueiros (rubber tappers), *A. phalerata* is a species for food, craft and construction materials, and also as "bait" for hunting animals that feed on the fallen fruits. The dried fruits have also historically been used by Seringueiros for producing smoke for the coagulation of *Hevea* latex (Pesce, 1941). The dried endocarp, or nut, like that of *A. speciosa,* can also be used to make a good quality charcoal. Another practice described by a few individuals was the gathering of *A. phalerata* fruits that contained the larva of a certain beetle. These fruits were cracked to retrieve the larvae, which are consumed as a delicacy.

Leaves:

Figure 2.4: Shelter with thatching made from *A. phalerata* leaves.

The main use of the leaves of *A. phalerata* is for thatching roofs on rural shelters (Figure 2.4). In urban areas during the period known as "festas juninas", it is a popular tradition to construct and decorate party areas with leaves of *A. phaerata* and A. *butyracea*. As in many cultures, the use of palm thatching as a roofing material has been substituted by modern materials such as aluminum sheeting. While still practiced, it has become much less common to find homes using *A. phalerata* for roofing.

Other Regions:

The uses of *A. phalerata* are similar in almost every area that the plant is found. In other regions of Brazil, Pio Correa (1984) cites the use of the dried epicarp of the fruit for the production of smoke during the "smoking" of rubber; the edible kernel is used to make a type of bread called "bró" as well as a rough farina for use in times of scarcity; the leaves serve as thatching and as forage for horses, the palm heart is edible, and the

trunk is used in rural construction. Native Indians extract starch from the mesocarp (fruit pulp) and edible oil from the endosperm (kernel) of the fruits.

In Bolivia, the leaves are also used as thatching, which can last as long as seven years, as well as in making baskets and fans (Balslev and Moraes, 1989). Palm hearts and the fruit are eaten raw, as well as oil from the fruit. The ash of the peduncular bract is chewed together with coca leaves (Moraes et al., 1996). Cardenas (1989) cites the use of the leaves in the covering of houses and the trunk in the construction of hunting implements such as bows, arrows and darts.

In Columbia the kernels are also used for oil extraction (Galeano and Bernal, 1987). Mejia (1988), studying the use of palms in communities near the river Ucayali in the Peruvian Amazon, noted that the majority of habitations, located in areas periodically inundated by rivers, had roofs constructed of leaves of *A. phalerata*. Mejia (1988) also notes that the larva of the beetle Rynchophorus, which grow inside of fruits that fall to the ground, are used as a food in local habitations.

Oil Extraction:

Extraction of the kernel for oil is a very time consuming and strenuous process. After the mesocarp is removed, the seed must be cracked using a hammer then boiled in water to release the oil, which is skimmed from the surface. The resulting light yellow oil can be sold at approximately US $15.00 per liter (Moraes et al, 1996), making the process profitable. The kernel of *A. phalerata* contains 66 - 69.5% oil, the highest recorded so far for any palm (Moraes et. al. 1996). Both mature and immature fruits can be used for oil extraction. The limitation to oil production is breaking the endocarp (nut) of the fruit, a

similar obstacle to that in *A. speciosa* (Babassu). Until today there has not been development of adequate equipment that can process the hard endocarp efficiently, and the species has been permanently classified in the journal Economic Botany as a species of grand potential for use in the future.

Medicinal Uses:

The medicinal uses of *A. phalerata* vary from place to place. In Brazil, liquid obtained from the immature kernel is recommended for the treatment of eye problems and the oil from the kernel is used to treat baldness in men (Pio Correa, 1984). Similarly, in Bolivia the kernel oil is reputed to have medicinal properties and is used cosmetically as a hair treatment and to prevent grey hair (Cardenas, 1989, Moraes et al.,1996). The Chácabo Indians of northwest Bolivia reportedly use a drink made from the leaves as a cure for diarrhea (Boom, 1988). Also the oil is taken orally to relieve pulmonary congestion and joint pain, and a juice from the boiled roots is used as a remedy for amoeba infection (Balslev and Moraes, 1989).

Chapter III

ANALYTICAL METHODS

Twenty mature *A. phalerata* palms from a selected site were chosen for this study. Observations of the fruiting stages of each palm were recorded and separated into five categories; ripe (fruits already on ground), almost ripe (about ready to fall), green fruits, flowering, and budding flowers. In order to quantify the characteristics of *A. phalerata*, ten nearly ripe stalks were harvested, brought to the lab, and allowed to ripen for several days. Weights and measurements were taken for the entire fresh stalk and individual fresh and dried fruit. Next, the fruits were separated into constituent parts and dried to calculate moisture content. The mesocarp (fruit pulp) and endosperm (kernel) were then ground into flours and basic nutritional analyses (humidity, ash, protein, lipids, and fiber content) were run. Extraction of the lipids from both mesocarp and kernel flours was carried out using three different solvents (to determine which solvent was the most efficient); hexane, petroleum ether, and sulfuric ether. Finally, the oils extracted with petroleum ether were characterized using a series of basic analysis for determination of the saponification, acidity, iodine, peroxide and density indexes. The following sections describe the methods used for each analysis.

Weights and Averages

Ten fresh *A. phalerata* fruit stalks (Figure 2.3) consisting of a range of sizes and fruit shapes were harvested for the study. The selection of varying sizes insured a robust average stalk characterization given morphological variations. Each stalk was brought back to the laboratory, numbered, and measured for length, diameter, and entire weight.

The quantity of fruits in each stalk was counted, and thirty fruits (ten from the top, middle, and bottom section, respectively) from each stalk were measured for length and width and then weighed.

Of the ten selected stalks, six ripened in sufficient time for the fruits to be used for nutritional analysis and oil extraction. From the six stalks, five kilogram mixed batches of fresh fruit were selected, weighed and then manually separated into the constituents of husk, mesocarp, and endocarp (seed). These were then each weighed to find the percentage of the entire fresh fruit they represented, and then dried at 60˚ C until constant weight to find water content. The method used to calculate water content for the entire fruit consisted of weighing twenty individual fresh fruits then drying them at 60 ˚C until constant weight.

Figure 3.1: Method commonly used for kernel extraction.

The kernel of the *A. phalerata* is difficult to remove from the fresh fruit; however, when dried the kernel separates from the seed and can be removed more easily. When

sufficiently dried, the fruits were weighed then cracked, using a machete and hammer, and the kernels were removed (Figure 3.1). Thus, the quantity of kernel per dried fruit was calculated and then using the measured water content, the percentage of seed per fresh fruit could be calculated. Finally, both the kernel and mesocarp were ground into flour using a meat grinder. The flour from each was used for the nutritional analyses and oil extraction.

Nutritional Analysis

Each of the analyses described below were run for samples of both mesocarp flour and kernel flour in nature (before the lipids were removed with solvent), as well as with samples that had lipids removed. All methods were carried out following those of Lutz 1985, with exception of the iodine which follows the method of the American Organic Chemists' Society (AOCS), 1990.

Humidity of Flour:

A freshly ground 5.0 gram sample was weighed and placed into a oven at 105˚ C. The sample was periodically removed, allowed to cool, and weighed on an analytical scale. This procedure was repeated until the weight was constant. The water content of the sample was determined by comparing the mass of the sample before and after it was dried using the following formula for determining water content, (Lutz, 1985):

$$(m_{fresh}-m_{dried})*100/m_{fresh} = \text{Humidity Value (\%)}$$

where; m_{fresh}= mass of fresh sample, and m_{dried}= mass of dried sample.

Ash:

The ash value corresponds to the residual obtained after a sample is incinerated. To determine ash content, a 5.0 g sample was placed in a porcelain crucible and put into a oven at 550˚ C. The crucible was periodically removed, cooled, and weighed on an analytical scale until the mass was constant. The ash value was determined by comparing the mass of the sample before and after incineration, using the following equation (Lutz, 1985):

$$m_{ash} * 100/m_{sample} = \text{Ash } (\%)$$

where: m_{ash} = mass of residuals after incineration, and m_{sample} = original mass of sample.

Protein:

The protein value was determined using the KJELDAHL method as defined in Lutz, 1985. This method is comprised of three steps: digestion, distillation and titration. The protein content of a sample is determined based on the amount of organic nitrogen (in the form of ammonia) distilled from a digested sample. The three basic steps of the method are as follows.

The sample is first digested in a solution of concentrated sulfuric acid and a catalyst of selenium sulfide, copper sulfate and sodium sulfate, which helps in the conversion of the amine nitrogen to ammonium ions. Next, the ammonium ions are converted into ammonia gas, heated and distilled. The ammonia gas is vented into a trapping solution of boric acid where it dissolves and becomes an ammonium ion once

again. Finally, the amount of the ammonia that has been trapped is determined by titration with a solution of HCl with a color indicator, and the amount of protein calculated. The step by step procedure is described below.

A freshly ground 0.5 g sample was placed in a 500 ml Kjeldahl digestion tube. Twenty milliliters of sulfuric acid (98% concentrated) were added, as well as 10 mg of the catalyst mixture of selenium dioxide, copper sulfate and sodium sulfate in a 1:10:100 proportion. The digestion tube was placed into the digestion equipment and left until the mixture turned clear (approximately 4 hours). It was removed from the heat and allowed to cool to room temperature.

Once cool, 250 ml of distilled water were added, and the remaining sulfuric acid was neutralized with sodium hydroxide 40%. The resulting solution was then distilled in the macro-Kjeldahl distiller (Figure 3.2) and decanted into a 250 ml Erlenmeyer flask containing 20 ml of boric acid (4%).The distilled solution was then titrated with 0.1 N HCl using a mixed color indicator (methyl red/methylene blue).

Figure 3.2 : Macro-Kjeldahl distiller used for distillation of ammonia.

The protein value was then calculated using the following equation for vegetable proteins (Lutz, 1985):

$$(V \times f \times 0.0014 \times 5.75 \times 100)/m_{sample} = \text{Protein Value (\%)}$$

where V= volume of 0.1N HCl used in the titration, f= factor of correction of HCl, and m_{sample} = mass of sample.

Lipid Content:

The extraction of lipids was carried out by the commonly used SOXHLET method. In the SOXHLET procedure, oil and fat from solid material are extracted by

repeated washing (percolating) a sample with an organic solvent, usually hexane or petroleum ether, under reflux in special glassware. In this study hexane and petroleum ether were both used to determine which solvent was best suited for extraction of lipids from the fruit pulp and seed of *A. phalerata.* A step by step description of the lipid extraction process is described below.

The extraction of lipids began with 5.0 g of ground sample, packed into a cellulose cartridge and covered with cotton. The cartridge was placed into a distillation flask and approximately 200 ml of solvent (hexane or petroleum ether) were added. The flask was then placed into a SOXHLET extraction system (Figure 3.3) and allowed to cycle through the system for a 6-8 hour period, to insure that all the lipids had been removed.

Figure 3.3: SOXLET extraction system processing *A. phalerata* mesocarp and kernel samples.

After the extraction, the flask containing the lipid residual was placed in an oven at 105˚ C for 30 minutes (or until all solvent had been evaporated). The sample was then removed, allowed to cool to room temperature, and then weighed.

The lipid content was calculated by comparing the mass of the original sample with the mass of the residual retained after distillation and removal of the solvent, using the following equation (Lutz, 1985):

$$m_{oil} \times 100/m_{sample} = \text{Lipid Content (\%)}$$

where m_{oil} = mass of oil extracted, and m_{sample} = mass of sample.

Fiber Content:

To find the fiber content, 1.5 g of ground sample were placed into a Kjeldahl digestion tube and heated until digested (about four hours), using a mixture of acetic acid, concentrated nitric acid, trichloroacetic anhydride acid, 70% solution of acetic acid and a catalyst solution of selenium dioxide, copper sulfate and sodium sulfate (proportion 1:10:100 by mass). The product was then filtered into a previously weighed porcelain filter crucible. This was then dried in an oven at 105 ˚C, cooled, and weighed on an analytical balance until constant mass. The fiber content was calculated by comparing the mass of the sample and the mass of the dried fiber remaining in the filter crucible using the following equation (Lutz, 1985):

$$m_{fiber} \times 100/m_{sample} = \text{Fiber Content (\%)}$$

where m_{fiber} = mass of fiber, and m_{sample} = mass of sample.

Oil Analysis

Saponification Index:

Saponification is the name given to the chemical reaction that occurs when a vegetable oil or animal fat is mixed with a strong alkali solution of water and potassium hydroxide. The term saponification literally translates to “soap making” after the Latin “sapo” meaning soap, and in the process of saponifcation there are two products generated: soap and glycerin.

The saponification index is defined as the number of milligrams of potassium hydroxide necessary to neutralize the fatty acids from the hydrolysis of a one gram sample of oil or fat. The process used to determine the saponification index is as follows.

A 2.0 g sample was weighed into a 250 ml bottle flask and 20 ml of potassium hydroxide alcohol solution 4% was added. This was placed into a reflux condenser and heated to boiling for 30 minutes, then removed from the heat and cooled to room temperature. Once cool, 2 drops of phenolphthalein were added, and the solution was titrated with chloridric acid 0.5N.

Next, a control was made using the same process. The difference between the volumes of chloridic acid used in the two titrations is equivalent to the quantity of potassium hydroxide used in saponification. The following formula was used to calculate the saponification index (Lutz, 1985).

$((V_{control} - V_{sample}) \times f \times 28))/m$ = Saponification Index

where: $V_{control}$ = volume (mL) of chloridic acid used in the control titration, V_{sample} = volume (mL) of chloridric acid used in the sample titration, f = factor of correction for chloridic acid 0.5 N, and m = mass of sample.

Acidity Index:

Stability and storage life are important characteristics to quantify for vegetable oils. The acidity, iodine, and peroxide indexes are quantitative measurements used to help determine these characteristics. The acidity index is defined as the number of milligrams of potassium hydroxide that is necessary to neutralize the free fatty acids in a one gram sample of oil. This index is determined using the relatively simple method described below.

To determine the acidity index 2.0 grams of sample were weighed in a 125 ml Erlenmeyer Flask, 25 ml of ether: ethyl alcohol (2:1) solution were added, then mixed vigorously. Next 2 drops of phenolphthalein indicator were added and the solution was titrated with sodium hydroxide solution 0.1N. The following formula was then used to calculate the acidity index (Lutz, 1985):

$$V \times f \times 5.61/m = \text{Acidity Index}$$

where: V= volume (ml) of sodium hydroxide solution 0.1 N used in the titration, f = factor of correction for the sodium hydroxide solution 0.1 N, and m = mass of sample.

Iodine Index:

The iodine index is used to determine the degree of saturation present in an oil; the higher the iodine index, the more unsaturation present. The method used to measure the iodine index is as follows.

First the sample was heated to between 68-71 ˚C and immediately weighed in a covered 500 ml flask. The recorded weight was then compared with the values given in Table 3.1.

Next, 20 ml of cyclohexane were added and stirred until the sample was completely dissolved. 25 ml of Wijs solution was added, the flask sealed and once more shaken. The solution was then placed in the dark at 25 +/- 5 ˚C, for a set amount of time determined by Table 3.1 (index<150, 1 hour; index>150, 2 hours). A control sample was then prepared following the same procedure, minus the oil.

After the solution was allowed to sit for the allotted time, 20 ml of KI solution were added as well as 100 ml of distilled water. This solution was then titrated with a 0.1 N solution of sodium trisulfate, until the yellow color of the solution disappeared. Next, 1-2 ml of starch solution were added and the titration continued until the blue color disappeared. The iodine index was then calculated using the following equation (AOCS, 1990):

$$(V_{control}\text{-}V_{sample}) \times N \times 12.69/m = \text{Iodine Index}$$

where; $V_{control}$ = volume (ml) of $Na_2S_2O_3$ spent in the control titration, V_{sample} = volume (ml) of $Na_2S_2O_3$ spent in the sample titration, m= mass of the sample, and N = normality of the $Na_2S_2O_3$ solution.

Table 3.1: Mass of sample and expected iodine indices.

Expected Iodine Index	Mass of sample, g ± 0.001
<5	3.000
5 – 20	1.000
21 – 50	0.400
51 – 100	0.200
101 -150	0.130
151 – 200	0.100

Peroxide Index:

The peroxide index, expressed as milliequivalents of peroxide per kilogram of fat, determines the degree of oxidation of an oil and should be calculated weekly to record how quickly an oil degrades or becomes rancid. The method used for finding the peroxide index is described below.

A 5.0 g sample was weighed into a 125 ml erlenmyer flask, and 30 ml of acetic-chloroform solution (3:2) were added, and mixed until the oil was dissolved. 0.5 ml of saturated potassium iodine solution were added and the solution was allowed to sit for exactly 1 minute. After one minute 30 ml of distilled water were added and then titrated while stirring with a sodium trisulfate solution 0.01N until the yellow color of the solution almost completely disappeared. Next, 0.5 ml of starch solution 1% was added and the titration continued until all of the iodine was liberated from the chloroform layer (solution turned blue), then drop by drop the titration was carried out until the blue color disappeared. A control was then prepared following the same procedure. The peroxide value was calculated using the following formula (Lutz, 1985):

$$(A-B) \times N \times 1000/P = \text{Peroxide index (meq/kg)}$$

where; A= ml of sodium trisulfate 0.01N spent in the sample titration, B= ml of sodium trisulfate 0.01N spent in the control titration, N = the true normalility of the sodium trisulfate solution, and P = mass of the sample (g).

Density:

The density of oils was determined using a picnometer in the following manner.

First a thermostatic bath was heated to 30˚ C, and the empty picnometer was weighed on an analytical balance. Next the picnometer was filled with the sample oil and placed into the thermostatic bath. After 20 minutes had elapsed the picnometer was removed, dried and weighed once more on an analytical balance. The density of the oil was then determined using the following formula:

$$m_{sample}/V_{picnometer} = \text{density (g/ml)}$$

where, m_{sample} = mass of the sample, $V_{picnometer}$ = volume of picnometer.

Chapter IV

RESULTS AND DISCUSSION

Nutrional Analysis and Oil Content of Fruits

Observations recorded for the twenty selected *A. phalerata* palms indicate that this species has a long fruiting season, and may produce fruits year round. The number of stalks and phase of growth for the twenty specimens are given in Table 4.1. An average of five stalks total per tree was recorded, with stalks ranging in maturation from ripe falling fruits, to unopened flowers. This range of fruit maturation was observed in several individual palms, indicating that a single palm is capable of producing fruit over extended periods. Observations and collections were made in late June, 2004.

Table 4.1: Observations of the number, and stage of maturation, of stalks for twenty selected *A. phalerata* palms.

Palm #	Ripe Stalks (Fruits on ground)	Stalks Almost Ripe	Green Stalks	Flowering Stalks	Unopened Flowers	Total
1	3	2	2	0	0	7
2	0	0	1	0	2	3
3	0	1	3	0	0	4
4	1	1	2	0	0	4
5	1	1	2	0	0	4
6	0	0	2	0	0	2
7	2	2	4	0	1	9
8	3	1	3	0	0	7
9	2	3	0	0	0	5
10	3	0	3	1	0	7
11	2	0	2	0	0	4
12	0	0	2	0	1	3
13	1	1	2	0	0	4
14	3	1	1	0	0	5
15	1	1	0	1	0	3
16	2	0	1	0	2	5
17	1	1	4	0	0	6
18	3	0	3	0	1	7
19	4	0	3	0	0	7

20	2	1	1	0	0	4
Average	1.7	0.8	2.05	0.1	0.35	5

The physical characteristics of the ten selected *A. phalerata* stalks are given in Table 4.2. From this table, as well as Figure 2.3, it is easily seen that significant variations in the number of fruits and size of individual stalks exist. The total number of fruits per stalk ranged from 90-480, with an average of 314 fruits. The total weight of fruit per stalk ranged from as little as 6.8 kg up to 27.7 kg and the average total weight of fruit for the ten stalks was 14.5 kg.

There was also significant variation in the number of fruits per stalk and their combined weight. For example, Stalk 3 had 480 fruits with a total weight of 14.4 kg while Stalk 6 had 475 fruits with a total weight of 27.7 kg. Thus, the fruits of Stalk 6 weighed nearly twice that of the fruits from Stalk 3. The rachis, or stem, size and weight varied also, but for the most part was proportional to the entire weight of the stalk.

Table 4.2: Weights anddimensions of ten selected *A. phalerata* fruit stalks.

Stalk	Length (cm)	Width (cm)	Circumference (cm)	Number of Fruits	Weight of Fruits (kg)	Rachis Length (cm)	Diameter Stem (cm)	Rachis Weight (kg)	Total Weight (kg)
1	62	32	91	261	16.222	51	6.0	1.720	17.942
2	63	28	85	412	17.053	52	5.4	1.265	18.318
3	56	29	82	480	14.399	48	5.2	1.570	15.969
4	59	29	79	413	12.409	54	4.6	1.355	13.764
5	54	29	79	141	12.619	36	4.6	0.885	13.504
6	83	39	103	475	27.723	74	6.1	4.455	32.178
7	40	26	70	90	7.844	36	5.0	0.705	8.549
8	42	25	74	109	6.848	38	6.0	0.980	7.828
9	79	34	105	467	21.477	76	6.3	3.505	24.982
10	56	25	74	299	8.774	49	4.5	1.050	9.824
Average	59	30	84	315	14.537	51	5.37	1.749	16.286

A total of 300 fruits were selected (thirty from each stalk) for recording the weights and dimensions of individual *A. phalerata* fruit. Within the 300 selected fruits a

large variation in weights existed. Fruits ranged from 20.2 g to 117.7 g, with an average weight of 57.8 g. Sizes ranged from 2.8cm to 5.3 cm in width and from 5.0 cm to 8.7 cm in length.

From the 300 selected fruits, two were selected from each stalk (a total of twenty) for use in measuring the moisture content of the entire fruit. The fruits were dried, individually weighed, and compared with the average fresh weight of 57.8g calculated above. The average dry weight of the twenty selected fruits was 28.3g. Comparing this with the average fresh weight, we find that moisture content of an entire fresh fruit is 51%.

Once dried, the twenty fruits were cracked and the kernels removed. Each fruit contained between one and four kernels, about 3 cm long by 1 cm wide (Figure 4.1) with a rich oily flavor similar to that of coconut. The kernels represented an average of 11.21 percent of the fruit by dry weight. Thus, if an average stalk contains 14.5 kg of fresh fruit, and 51 percent of this weight is moisture, then this amounts to 7.1 kg of dried fruit. If 11.21 percent of this dried weight is kernel, an average stalk will provide 0.796 kg of kernel, and if an average *A. phalerata* palm produces five stalks per year, total kernel production for one palm per year would equal 3.98 kg.

Figure 4.1: Seed content of *A. phalerata* fruit with close up of whole kernels.

Five kilogram mixed batches of whole fruits were hand processed to separate the fruit into constituent parts. During processing it was apparent that individual fruits varied greatly in the relative amounts of mesocarp (fruit pulp) and seed. Table 4.3 presents the percentages and moisture content that each constituent part comprised of the entire fruit. By weight the husk, mesocarp, and seed made up an average of 30.18, 20.31 and 46.36 percent of the entire fresh fruit, respectively. The small remainder unaccounted for consisted of the sepal cap which was discarded. When dried, the husk, mesocarp, and seed made up 22.86, 15.19 and 60.5 percent dry weight of the fruit, respectively. Moisture content of the separate parts was also calculated at this time with the husk, mesocarp, and seed containing 56.37, 55.71 and 27.15 percent water by fresh weight, respectively.

Table 4.3: Percentages of the constituent parts of *A. phalerata* fruit.

Portion of Fruit	% of Fresh Fruit	% of Dried Fruit	% Moisture
Husk	30.18	22.86	56.37
Mesocarp	20.31	15.19	55.71
Seed	46.36	60.5	27.15

Besides the kernel, the mesocarp also has considerable potential to be used for oil production. If the dried fruit contains 15.19 percent mesocarp, then an average stalk weighing 7.1 kg dried would yield 1.08 kg of mesocarp, and an average *A. phalerata* palm producing five stalks per year would produce 5.4 kg of mesocarp per year.

The basic nutritional characteristics of the prepared mesocarp and kernel flour of *A. phalerata* fruit are summarized in Table 4.4. The flours used were made from the previously dried mesocarp and kernels which reabsorbed moisture from the humid environment of Acre, hence the moisture content value for the flours are “in nature”.

The kernel contains 68.41 percent oil that is light yellow in color and has a slightly sweet odor. This value is similar to values reported by both Moraes el al. (1996) as well as Pesce (1941), which were 69.5% and 66%, respectively. The mesocarp contains 20.82 percent of orange yellow oil that is more viscous and opaque than the kernel oil. Figure 4.2 shows samples of both kernel and mesocarp oils.

Table 4.4: Basic nutritional analysis results for *A. phalerata* mesocarp and kernel flours.

	Moisture %	Ash %	Fiber %	Protein %	Lipids %
Kernel in Nature	3.56	2.00	-----	7.89	68.41
Kernal without Lipids	-----	3.73	52.38	14.26	-----
Mesocarp in Nature	7.33	4.02	-----	4.05	20.82
Mesocarp without Lipids	----	5.12	10.46	6.12	-----

Fiber analysis can only be run with samples which have already had lipids removed, thus the lack of data in Table 4.4 for fiber content on samples “in nature”. The lipid content after extraction was so insignificant that this value was also not reported in Table 4.4. One important point worth noting is the protein and ash content in the samples containing lipids, and those with lipids removed. The percentages of proteins and ash increase simply because when the lipids have been removed the protein and ash portion make up a larger fraction of the sample. The protein content of the kernel and mesocarp after the lipids are removed give these flours the potential to be used as fodder for livestock (Pesce, 1941).

Figure 4.2: Mesocarp and kernel oil of *A. phalerata,*, showing color and opacity.

Taking the lipid content of *A. phalerata* mesocarp and kernel presented in Table 4.4, we can estimate the quantity of oil produced per palm per year. If the dry kernel contains 68.41 percent oil, and an average stalk is estimated to produce 0.796 kg of kernel by dry weight, then an average stalk would provide 0.545 kg of oil. Multiplying this by five (the average number of stalks per tree), we find that one palm could produce 2.72 kg of kernel oil per year. Similarly, mesocarp oil per stalk and per palm is estimated to be 1.12 kg and 5.62 kg, respectively.

Moraes et al (1996) estimates that one hectare can support between 115 and 236 mature fruiting *A. phalerata* palms depending on spacing and planting patterns. Using this estimate one hectare of *A. phalerata* could produce between 313.8 and 641.9 kilograms of kernel oil and 646.3-1326.3 kilograms of mesocarp oil per year. Combined this equals 860 to 1968 kilograms of oil per hectare per year. For a comparison with other common oil crop yields refer to Table 5.1. The value estimated by Moraes et al., which was between 1173 and 2407 kilograms of oil per hectare, is significantly different. However, the study conducted by Moraes et al., 1996, was carried out using a “small random sample of fruits” bought at a local market (presumably larger and more desirable

fruits), while this study purposely sought a robust characterization and included a variety of stalks and fruit sizes.

The oil production estimates from this study were made from a wide selection of naturally occurring *A. phalerata* palms. Thus there was no selection for favorable varieties as would be practiced if the palms were planted as a crop. It is therefore reasonable to assume that with selection for high yield strains, the oil producing capacity of *A. phalerata* could increase significantly in comparison to the values estimated here.

Oil Extraction and Analysis

Due to the relatively small quantity of material available for this research, extraction of both the mesocarp and kernel oils was carried out using solvent rather than the commonly used methods of pressing, or boiling and skimming. During the extraction process three separate solvents were experimented with to determine which was more suitable for use in extraction. The first used was hexane, a solvent commonly used in industrial vegetable oil production. The hexane proved very difficult to evaporate from both mesocarp and kernel oils, even when done under vacuum. Indeed, it was finally evaporated from the oil only after placing the sample into an oven at 100 ˚C for three days! This effectively burned the oil, making it unsuitable for analysis. The second solvent used was sulfuric ether, which worked well with the kernel oil, however it reacted strangely with the mesocarp oil to form a thick coagulation within the oil. Petroleum ether proved to be the most favorable solvent, evaporating easily and providing good samples of both mesocarp and kernel oil.

The oil analyses that were conducted provide a basic idea of structure and quality of the oils. The iodine and saponification indices yield information on the structure of the oils, while the acidity and peroxide indices indicate the quality. Results for the oil analyses for both mesocarp and kernel oil of *A. phalerata* are presented in Table 4.5. To complement these results, Table 4.6 from another study, provides results of basic nutritional analysis of the mesocarp and kernel oils. It can be seen from Table 4.5 that the oils have about the same density, but differ significantly in all other values. It can be seen that the nutritional characteristics of the kernel and mesocarp oils of *A. phalerata* differ significantly with the kernel oil having a much larger percentage of fats and solubles (Table 4.6).

Table 4.5: Basic oil analyses results for A. phalerata mesocarp and kernel oils.

	Mesocarp Oil	Kernel Oil
Density (g/ml)	1.08	1.10
Saponification (mg KOH/g)	171.59	233.28
Acidity (mg KOH/g)	9.91	0.69
Iodine (mg I/ 100g oil)	51.00	19.96
Peroxide (meq/kg)	29.54	4.01

The iodine, acidity, and peroxide indices are important values in determining the stability and shelf life of an oil, as well as if an oil is suitable for use as a fuel in internal combustion engines. The relatively low peroxide and acidity values in Table 4.5 indicate that neither the mesocarp or kernel oil had degraded significantly at the time the analyses were conducted.

Table 4.6: Results of bromatoligical analysis of kernel and mesocarp oil of *A. phalerata,* values given as percentages. After: Moraes et al., 1996

	Ash	Fibers	Fats	Proteins	Soluble Extract
Kernel	6.4	6.7	59.9	9.8	17.2
Mesocarp	12.7	46.5	29.5	6.3	5.0

Some oils have the potential to be used directly in diesel engines without being converted into biodiesel. However one of the major problems associated with using oils and fats as a fuel is the potential for the oil to polymerize when combusted. This process occurs naturally when the double (and sometimes triple) bonds in the unsaturated oil molecules are broken by atmospheric oxygen and converted to peroxides. Cross linking can then occur at these sites and the oil is irreversibly polymerized into a plastic-like solid (Cole et al., 1978). This process is greatly accelerated under the high temperatures in internal combustion engines, and an engine can quickly become gummed-up with the polymerized oil.

The iodine index is the traditional measure of the degree of bonds in an oil available for polymerization. The higher the iodine index the more unsaturated (the greater the number of double bonds) the oil and the higher the potential for polymerization. Generally, an iodine index of less than 25 is required if straight oil is to be used for long-term applications in unmodified diesel engines (Calais and Clark, 1999). From Table 4.5 it can be seen that the kernel oil from *A. phalerata* has an iodine index value of 19.96, indicating that this oil may have the potential to be used directly in diesel engines without modification. Regardless of the potential as a fuel, the similarities that the mesocarp and kernel oils of *A. phalerata* have with other palm and palm kernel oils suggest they both are suitable for biodiesel production.

The percentages of fatty acids of both the kernel and mesocarp oils of *A. phalerata* and other palms are given in Table 4.7. From this table it can be seen that both the mesocarp and kernel oils of *A. phalerata* are relatively low in double bonded fatty

acids. This observation verifies the lower iodine index values given in Table 4.5 (recall that a high iodine index indicates a higher number of double bonds). Also from Table 4.7 we can see that both the kernel and mesocarp oils are relatively high in oleic acids (18:1), with the value for mesocarp oil similar to that of the mesocarp oil from *Elaeis guineensis* (African Oil Palm). The largest percentage (36.4%) of fatty acids in the kernel oil of *A. phalerata* is comprised of lauric acids (12:0). Oleic and lauric acids are both important products with many applications in food, cosmetic, and chemical industries.

Table 4.7: Percentages of fatty acids of kernel fat and mesocarp oil of *A. phalerata* and other palms. (After Moraes et al., 1996)

	% fatty acid												
	Length of fatty acid and number of double bonds												
	6:0	8:0	10:0	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:0
Elaeis guineensis[a]													
Kernel	tr.-1.5	3-5	3-7	40-52	14-18	7-9	----	1-3	tr.-1	11-19	0.5-2	----	----
Mesocarp	----	----	----	----	0.5-6	32-47	----	2-8	40-52	5-11	----	----	----
Cocos nucifera[a]													
	0.08	5-9	6-10	44-52	13-19	8-11	0-1	1-3	5-8	tr.-2.5	----	----	----
Attalea colenda[b]													
Kernel	----	4.5	4.8	47.2	16.1	7.3	----	2.8	13.5	3.0	0	0	----
Attalea speciosa[c]													
Kernel	----	4.1	7.6	45.1	16.5	5.8	----	5.5	11.9	2.8	----	----	----
Attalea phalerata[d]													
Kernel	tr.	4.4	4.6	36.4	16.6	10.2	----	4.2	20.9	3.1	----	----	----
Mesocarp	----	----	0.5	7.3	11.0	21.9	0.2	3.8	47.5	4.8	3.0	Tr.	tr.
kernel[e]	----	5.1	4.2	28.5	14.6	11.5	----	4.2	26.8	4.7	----	----	----

Source: Berger and Ong 1985: source: Blicher-Mathiesen and Balslev 1990: source: Hilditch and Williams 1964: source: Moraes Borchsenius and Blicher-Mathiesen 1996:source Lleras and Coradin 1988. (tr. = trace; ------- = not investigated; 6:0 = Caprioc; 8:0 = Caprylic; 10:0 = Capric; 12:0 = Lauric; 14:0 = Myristic; 16:0 = Palmitic; 18:0 = Stearic; 18:1 = Oleic; 18:2 = Linoleic; 18.3 = alpha-Linolenic; 20:0 = Arachidic; 22:0 = Behenic)

The mesocarp and kernel oils of *A. phalerata* are similar to the kernel oil of *A. speciosa* (Babassu related palm already used as a significant source of oil in other

Brazilian States), and *E. guineensis* (Pesce, 1941; Moraes et al., 1996). These observations suggest that mesocarp and kernel oils from *A. phalerata* may share many of the same applications as the oils from *A. speciosa* and *E. guineensis*, including uses as food grade oil and in biodiesel production.

Chapter V

A COMPARISON OF BIODIESEL AND PETROLEUM DIESEL: POSSIBLE EFFECTS ON BIOGEOCHMEISTRY

While the research work of this paper focuses on the potential for *A. phalerata* to be used as a source of oil for the production of biodiesel, it is important that we also take a look at the potential that biodeisel has globally as a fuel. This chapter will compare and contrast the characteristics of biodiesel, with that of its fossil fuel counterpart, petroleum diesel. First, the broad similarities and differences of the origins of these two fuels and how they are made are discussed. Then the focus turns to the major chemical compounds these fuels release when combusted, and the subsequent influences that large scale use may have on the reservoirs of several elemental biogeochemical cycles. The last section explores the possible implications and influences that large-scale biodiesel production may have on global systems.

Origins

Sunlight is the ultimate source of energy fueling biological activity on this planet. Solar energy plays an important role in every biogeochemical cycle. In fact, without sunlight there would be no "bio" in biogeochemical.

Petroleum:

In essence, fossil fuels are sunlight that was captured and stored hundreds of millions of years ago in the remains of organisms capable of photosynthesis. These organic remains, hereafter referred to as organic matter, were subjected to high temperatures and pressures within the earth where they were subsequently turned into the fossil fuels of coal, oil and gas. Oil and gas formed principally from the altered remains of phytoplankton in sediments on the ocean floors. Lipids within this organic matter are very likely the main source for petroleum deposits (Hunt, 1979). Oil and gas deposits were formed within deeply buried marine sediments by three major processes: diagenesis, catagenesis and metamorphism (Tissot and Welte, 1978; Hunt, 1979). Coal deposits are derived mainly from terrestrial plant matter that was deposited in swampy environments (Mackenzie, 2003). In either petroleum or coal formation, it is important to note that anaerobic conditions and rapid depositional rates are crucial for the preservation of the organic matter deposited. (Tissot and Welte, 1978).

Once a petroleum deposit has been located, drilled, pumped and transported to a refinery, the crude oil can then be processed. Distillation is the principle process used for converting crude oil into its various petroleum products (Hunt, 1979). During distillation crude oil is heated to its boiling point inside a distillation tower, and the oil vapors rise up the center of the tower where they cool and condense. Gutters are placed at different levels to catch the different grades of oil that condense (Tickell, 2000). Diesel, kerosene and gasoline are all produced by distillation, (Figure 5.1).

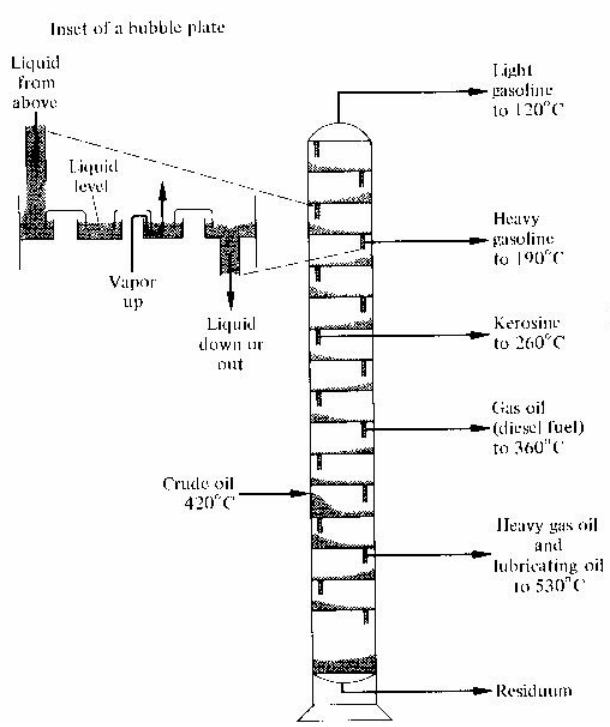

Figure 5.1: Diagram of a petroleum distillation tower showing the condensation levels and temperatures of the various products. After Hunt, 1979.

Biodiesel

The original precursors of fossil fuels are the same for biodiesel; the lipids (fats or oils) of photosynthetic organisms (in biodiesel animal fat can also be used). However, in the production of vegetable oil, there are no geological processes involved and the time scale for production is in months or years (Tickell, 2000), as opposed to hundreds of millennia. Many plant species produce large amounts of oils and store them in their seeds. Vegetable oil is most commonly obtained by use of a press that squeezes the oil

from the seed. Numerous oil-producing crops are suitable for biodiesel production. A per-hectare annual yield is given for many common oil crops in Table 5.1.

Table 5.1: List of oil-producing crops showing common and Latin names as well as average oil yield in kg/hectare/year. Note: Figures are averages, harvests vary with region and subspecies. After Tickell, 2000.

Plant	Latin Name	Kg Oil/Hectare	Plant	Latin Name	Kg Oil/Hectare
Corn	Zea mays	145	tung oil tree	Aleurites fondii	790
cashew nut	Americardium occidentale	148	Sunflower	Helianthus annuus	800
Oat	Avena sativa	183	Cocoa	Theobroma cacao	863
Palm	Erthea salvadorinsis	189	Peanut	Arachis hypogaea	890
Lupine	Lupinus albus	195	opium poppy	Papaver somniferum	978
rubber seed	Hevea brasiliensis	217	Rapeseed	Brassica napus	1000
Kenaf	Hibiscus cannabinus	230	olive tree	Olea europea	1019
Calendula	Calendula officinalis	256	Piassava	Attalea funifera	1112
Cotton	Gossypium hirsutum	273	gopher plant	Eurphorbia lathyris	1119
Hemp	Cannabis sativa	305	castor bean	Ricinus communis	1188
Soybean	Glysine max	375	Bacuri	Platonia insignis	1197
Coffee	Coffea Arabica	386	Pecan	Carya illinoensis	1505
Linseed	Linum usitatissimum	402	Jojoba	Simmondsia chinensis	1528
Hazelnut	Corylus avellana	405	babassu palm	Orbignya martiana	1541
Euphorbia	Euphorbia lagaseae	440	Jatropha	Jatropha curcas	1590
pumpkin seed	Cucurbita pepo	449	macadamia nut	Macadamia terniflora	1887
Coriander	Coriandrum sativa	450	brazil nut	Bertholletia excelsa	2010
Mustard	Brassica alba	481	Avocado	Persea americana	2217
Camelina	Camelina sativa	490	Coconut	Cocos nucifera	2260
Sesame	Sesamum indicum	585	Oiticia	Licania rigida	2520
Crambe	Crambe abyssinica	589	buriti palm	Mauritia flexuosa	2743
Safflower	Cartamus tinctorius	655	Pequi	Caryocar brasiliense	3142
buffalo gourd	Cucurbita foetidissima	665	macauba palm	Acrocomia aculeata	3775
Rice	Oriza sativa L	696	oil palm	Elaeis guineensis	5000

Another source of biodiesel that may prove to be much more productive than terrestrial plants is the oils produced by algae. According to a study by researchers at the National Renewable Energy Laboratory, production of algae reached 50 grams per square meter per day in 1000 square meter ponds (Sheehan et al., 1998). This equates to 50 kilograms of algae per day per pond. The diatom algae used in this experiment were approximately 50 percent oil by weight. Given this high oil content, one 1000 square meter pond could produce up to 9,125 kg of oil per year (Tickell, 2000). In contrast, the

African oil palm, the highest producing terrestrial oil crop, has an annual yield of 5000 kg/hectare (Table 5.1). Thus, algae could produce nearly twice as much oil in a tenth of the space.

Transesterification is the process used in converting vegetable oil into biodiesel. Vegetable oil is a triglyceride, a molecule consisting of three esters (hydrocarbon chains) attached to a glycerin molecule (Figure 5.2). In the process of transesterification, vegetable oil is mixed with an alcohol (ethanol or methanol) and a catalyst (sodium hydroxide (NaOH), or potassium hydroxide (KOH)). The catalyst breaks the three esters from the glycerin molecule, where they are free to bond with the alcohol to form three alkyl esters, while the catalyst bonds with the glycerin to form glycerin soap which settles out of solution (Tickell, 2000).

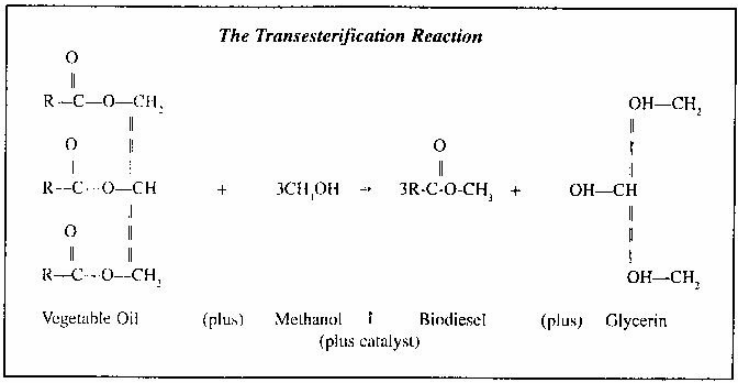

Figure 5.2: Simple depiction of the transesterification reaction using methanol, note R represents the ester chains. (Tickle, 2000).

Biodiesel and petroleum come from a similar source in regard to their original precursors, lipids. While biodiesel production currently uses mainly vegetable oil from terrestrial plants, algae may prove to be the only feasible way to produce quantities near the levels needed to match the amount of petroleum diesel used today. Given that the

majority of petroleum deposits are believed to originate from the oils produced by phytoplankton, further research into algal oil production may prove to be very useful.

Composition and Combustion

Petroleum

Table 5.2: Average chemical composition of several natural substances. (Hunt, 1979)

Elemental composition in weight percent					
	C	H	S	N	O
Carbohydrates	44	6	--	--	50
Lignin	63	5	0.1	0.3	31.6
Proteins	53	7	1	17	22
Lipids	76	12	--	--	12
Petroleum	85	13	1	0.5	0.5

The average chemical composition of petroleum is 85 percent carbon, 13 percent hydrogen, and 2 percent S, N and O (Table 5.2). Due to the high degree of alteration of organic matter during the processes of diagenesis, catagenesis, and metamorphism, these elements (C, H, S, N, and O) occur in many different, complex, molecular forms. In the light gas oils, oils used in diesel and jet fuels, the "composition of the gas oil fraction is known in terms of the grouping of molecular types; however, it is so complex that only a few hydrocarbons have been identified in its total range (C_{14}-C_{25})" (Hunt, 1979). The molecular types referred to by Hunt are the paraffins, cycloparaffins (or naphthenes), aromatics, and the nonhydrocarbons (compounds containing N, S, or O in the molecule). Following is a brief description of each molecular type.

Napthenes and paraffins are referred to as saturated hydrocarbons, which means that all available carbon bonds in these compounds are occupied by hydrogen. Napthenes are the most abundant compounds in crude oil (and in diesel), followed by paraffins and

the aromatics (Hunt, 1979). The aromatics are hydrocarbons that contain at least one benzene ring. Several of these compounds are known potent carcinogens, and most aromatics are toxic to living organisms (Hunt, 1979). The nonhydrocarbons as previously stated make up a small fraction of diesel content, and are compounds that contain a nitrogen, sulfur, or oxygen atom.

When combusted, parafins, napthenes, and nonhydrocarbons can be released directly, most however react to form other complex compounds that are emitted in the gaseous phase or as particulate matter. Discussion of these numerous compounds is far beyond the scope of this paper. Thus, when comparing the emissions of petroleum and biodiesel, only CO_2, CO, SO_x, NO_x and particulate matter will be discussed in the following sections.

Biodiesel

The average elemental composition of lipids is different from petroleum. Lipids are comprised of 76 percent carbon, 12 percent hydrogen, and 12 percent oxygen (Table 5.2). Lipids, and biodiesel fuel from lipids, contain no nitrogen or sulfur (Tickell, 2000). Sulfur in petroleum originates mainly from two sources. The first is from the activities of sulfate-reducing organisms found in the anaerobic sediment environment, and the second is from high temperature reactions with reservoir rocks within the earth (Hunt,1979).

When combusted in an engine, biodiesel emissions are significantly lower than those of petroleum diesel, with the exception of NO_x compounds (Munack et al., 2001). NO_x compounds emitted from biodiesel are actually slightly higher than those of petroleum diesel, (Munack et al., 2001). Oddly enough, biodiesel contains no nitrogen,

thus the NO_x emissions must be due solely to reactions with atmospheric N_2 during combustion. However, use of catalytic converters and reduction of the combustion temperature by retarding engine timing can lower NO_x emissions to levels below those of petroleum diesel (Tickell, 200; Munack et al., 2001). Tailpipe emissions for several important greenhouse gasses and particulate matter are listed in Table 5.3. The first and third columns compare 100 percent petroleum diesel and biodiesel. Note that the emissions of CO_2, SO_x, and PM are lower for 100 percent biodiesel than those for petroleum diesel. The carbon dioxide in biomass (Table 5.3, row 2) refers to CO_2 involved in respiration and decay of the crops grown for biodiesel.

Table 5.3: Effect of Biodiesel on Tailpipe Emissions (g/bhp-h). (Sheehan et al, 1998.)

Emission	Diesel Fuel Baseline	20% Biodiesel Blend	100% Neat Biodiesel
Carbon Dioxide (fossil)	633.28	534.10	136.45
Carbon Dioxide (biomass)	0	108.7	543.34
Carbon Monoxide	1.2	1.089	0.6452
Hydrocarbons	0.1	0.09265	0.06327
Particulate Matter (PM10)	0.08	0.0691	0.02554
Sulfur Oxides (as SO_2)	0.17	0.14	0
Nitrogen Oxides (as NO_2)	4.8	4.885	5.227

In a 1998 study funded by the U.S. Department of Agriculture and the U.S. Department of Energy, researchers compared the overall lifecycles of biodiesel and petroleum diesel. This study examined and attempted to quantify the energy balance, effects on greenhouse gas emissions, and the effects on the generation of air, water, and solid waste pollutants for every operation needed to make biodiesel and diesel fuel (Sheehan et. all, 1998). An example of a lifecycle used by Sheehan et al. (1998) is shown

in Figure 5.3, the figure depicts the biomass carbon balance for biodiesel made from soybean oil.

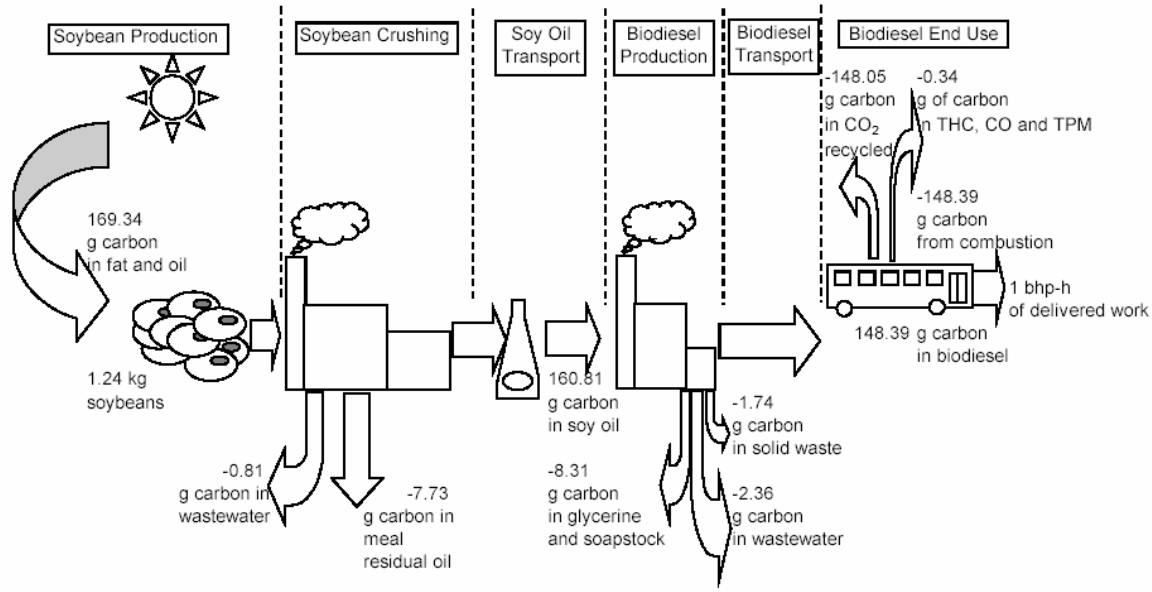

Figure 5.3: Biomass Carbon Balance for the Biodiesel life cycle. (Sheehan et al, 1998)

The results of this study showed that lifecycle emissions from biodiesel for most greenhouse gases and PM are considerably lower than those of petroleum diesel. CO_2, CO, SO_x, and PM emissions from biodiesel were found to be 78.45 percent, 35 percent, 8 percent, and 32 percent , respectively, those of petroleum diesel's lifecycle emissions (Sheehan et al., 1998). Consistent with the study of Munack et al. 2001, this study also found that NO_x emissions from biodiesel are slightly higher than those from petroleum diesel. The source of sulfur and fossil carbon in the biodiesel lifecycle was attributed by this study to the use of fossil fuels in one or more stages of biodiesel production.

Biogeochemical Influences

Petroleum:

If we examine the lifecycle of fossil fuel use, we can see that it is a process that affects biogeochemical cycling from start to finish. The most obvious cycles involved are the carbon, sulfur, and nitrogen cycles. However, due to the integrated nature of biogeochemistry, it is likely that the perturbation of these cycles affects other elemental cycles in ways of which we are not yet aware. Furthermore, it is not only the combustion of fossil fuels that affects biogeochemical cycles, but also processes for obtaining, transporting and refining petroleum involve and impact biogeochemical cycles. The biodegradability and toxicity of petroleum products affect biological activity (Nauss, 1997) and alter the rate at which the elements that make up these materials can reenter their natural cycle. For example, oil spills, and the manner in which humans dispose of the multitude of petroleum products that are in wide use in industrialized areas affect the natural cycling pathways for their associated elements.

As stated earlier, fossil fuels are comprised mostly of carbon that has been sequestered in the Earth over a time scale of hundreds of thousands of years or more. This "sink" makes up part of the biogeochemical cycle of carbon. By using fossil fuels, we are removing carbon from one reservoir and putting it into another, thus altering the natural pathways of the carbon cycle. Carbon monoxide and CO_2 are important carbon compounds that are released by combustion. CO has a short residence time in the atmosphere, reacting readily with the hydroxyl radical to form CO_2. For this reason CO is often included as part of the CO_2 flux in most accounts of the global carbon cycle (Schlesinger, 1991). Today it is a widely accepted fact that fossil fuel combustion is

responsible for the recent rapid increase of carbon dioxide in the atmosphere. Carbon dioxide is a known greenhouse gas and its rapid accumulation in the atmosphere, due to fossil fuel combustion, may prove to have far reaching effects on many global processes.

In regions of the world dominated by large industrialized cities (as well as areas downwind of them), combustion of fossil fuels has been directly linked to increased levels of NO_X and SO_X gases. This increase in sulfur and nitrogen compounds represents two more disruptions of the biogeochemical cycles. Nitrogen in the atmosphere, in the form of N_2, is oxidized during combustion (Tickell, 2000), thus altering the natural state of N in the atmosphere allowing it to fall out as acid deposition, or react in the atmosphere to form tropospheric ozone (Mackenzie, 2003). In the use of fossil fuels, sulfur, as with carbon, is removed from a relatively stationary reservoir in petroleum and released into the atmosphere as SO_x compounds. These compounds can also form acid deposition, or sulfate aerosols that reflect incoming solar radiation, thus having a possible cooling effect on the planet (Mackenzie, 2003).

The above listed examples of the influence of fossil fuel combustion on biogeochemistry provide a glimpse into how interconnected all of the global elemental cycles are. Each reaction involves elements from different cycles, and each product from each reaction may in turn interact with other elements. In this sense it is very difficult to define where the effect of one anthropogenic activity on biogeochemistry ends. Given this complexity it is extremely important that we understand the influences that developing other fuel sources (such as biodiesel) may have on biogeochemical cycling .

Biodiesel:

Biodiesel production and use, compared to that of petroleum diesel, may prove to have less impact on some parts of the biogeochemical cycles and more on others. Many of these effects must be hypothesized due to the fact that biodiesel has not yet been used in quantities great enough to link it to changes in the environment.

Petroleum diesel combustion releases "stored" carbon into the atmosphere, which results in an increase of carbon to the atmospheric reservoir, (and subsequently other reservoirs such as the ocean). The carbon that biodiesel releases upon combustion does not result in an increase in atmospheric CO_2 (Tickell, 2000). This is due to the fact that within the carbon cycle, biodiesel combustion represents a closed loop process. By using carbon already present in the cycle, biodiesel provides no net flux of CO_2 into the atmosphere. The same amount of CO_2 released to the atmosphere when biodiesel is combusted is taken up again by plants during photosynthesis.

Because there is no sulfur present in biodiesel, there are no SO_X compounds released during combustion. Thus if substituted, or mixed with petroleum diesel, biodiesel may prove to have a positive influence on reducing acid deposition and sulfate aerosols. This may result in less anthropogenic impact on the natural cycling of sulfur, although possibly may have a negative affect on solar reflectivity in the atmosphere due to the decrease in SO_X compounds that would be released from combusting pure petroleum diesel.

The slight increase of NO_X compounds from the use of biodiesel may prove to increase the amounts of tropospheric ozone, as well as acid deposition around large industrialized cities. However, these emissions may be decreased with proper engine

adjustments. Thus the influence on the nitrogen atmospheric cycle due to emissions may be equal to, or slightly higher than, the effect from petroleum diesel use.

The emissions from biodiesel could potentially affect atmospheric reservoirs of carbon and sulfur less than emissions from petroleum diesel. However, the processes involved in producing biodiesel may impact other areas of the biogeochemical cycles to a greater degree. In order to produce large enough quantities of biodiesel, there must be a large increase in the amount of land used for agricultural production. This increase in agriculture will undoubtedly create a need for substantial amounts of fertilizer, and increase water consumption. Increased fertilizer use and water consumption could impact the hydrologic cycle, soil chemistry, distribution of vegetation, and nutrient cycling significantly.

For example, in the life cycle study discussed previously, it was found that the lifecycle consumption of water for soybean biodiesel is three orders of magnitude greater than that for petroleum diesel (Sheehan et al, 1998). Thus, increases in water consumption could prove to be enormous when producing biodiesel in large enough quantities to satisfy transportation needs. Such an increase in water consumption may result in alteration of river flow, as with the Colorado River (Mackenzie, 2003), and limit the possibility of agriculture in some regions downstream. Alteration of river flow would subsequently influence other areas of biogeochemistry.

Intensive agricultural practices can affect nutrient cycling in numerous ways. Growing high yield crops often depletes soil nutrient levels making the soil unsuitable for future crops, and creating the need for fertilizer addition. By introducing synthetic fertilizers, high in N and P, to the soil, there is an increase of these nutrients in runoff

waters, groundwaters, and with respect to N, an increased flux to the atmosphere in the form of N_2O due to microbial activity in croplands (Mackenzie, 2003).

The need for, and production of, fertilizers represents an indirect way in which biodiesel production may affect the global cycling of N and P. Both of these nutrients must be attained from available reservoirs. Nitrogen is taken from the atmosphere using the Haber-Bosch process and made available for use by plants and other organisms, while phosphorus fertilizers are obtained mainly from mining ores (Schlesinger, 1991; Mackenzie, 2003). Growing crops for biodiesel will undoubtedly increase the present rate of production and consumption of these fertilizers, thus increasing anthropogenic influences on the N and P cycles.

Net primary production (NPP) could also be significantly affected by the large scale use of biodiesel. In a recent study on biofuel use, it was estimated that the amount of carbon used in fossil fuels in 1997 was more than 400 times that of the amount sequestered in current NPP (Dukes, 2003). With large increases in agricultural lands for oil crops, NPP would likely be altered, human consumption of NPP would increase, and this would place addition burdens on plant and animal life.

CHAPTER VI

CONCLUSIONS

Due to the finite reserves of fossil fuels, the use and development of alternative energies will increase in the coming decades. While wind, solar, and hydroelectric are ideal alternative energy sources for electricity generation, none of these have proved suitable for use in the transportation of goods and people. Biodiesel can be used in diesel engines without conversion; this makes it an ideal alternative fuel for use in the transportation industry. Also, the relatively simple process used in producing biodiesel makes it an excellent alternative energy source for rural populations that may not have the access to, or the monetary resources for, other alternative energies. In the coming years, the growth of oil producing crops will increase to meet the demand for transportation fuels in both large industry and small rural communities.

This expected rise in the use of biodiesel will increase the demand for already established oil crops as well as new crops such as algae. This will result in more land area set aside for production. In some regions, such as the Southwestern Amazon, numerous naturally occurring palm species exist in large numbers and have the potential to be used in a sustainable approach to development as well as energy production. Many of these species remain entirely underutilized by local populations. The palm *Attalea phalerata* is one such species; this palm can provide a range of useful products including food, fuel, and shelter. Wild stands of *A. phalerata* have been shown to be capable of producing significant quantities of oil. The mesocarp and kernel oils from *A. phalerata* are similar to the oils from the African Oil palm, and the Babassu; two species used as oil crops that have oils suitable for biodiesel production.

Up until present time, the production of oil from *A phalerata,* (and *A. speciosa*) has been limited due to the difficulty in extracting the kernel. It is likely that this will remain the case until equipment has been developed that can efficiently extract the kernel from the hard shell of the seed.

Globally, increases in biodiesel use as a substitute for petroleum may lessen the quantities of combustion emissions to the atmosphere of CO_2, SO_X, and PM from fossil fuels, with a slight increase in the flux of NO_X compounds. Engine adjustment and use of catalytic converters can reduce these NO_X emissions. Thus, biodiesel combustion may have an overall smaller impact on atmospheric reservoirs of certain compounds than petroleum diesel combustion. However, due to increases in the amount of land used for oil crops, and the quantities of water and fertilizers used in the overall lifecycle of biodiesel production, impacts on soil health, and hydrologic and nutrient cycles could be significant in areas practicing large scale intensive cropping.

With this in mind, it is crucial that societies take a sustainable approach to the issue of biodiesel production. Species such as *A. phalerata* can play a very important role, especially in rural settings. Small diversified systems of production will not only ensure the self sufficiency of communities, but will also lessen the stresses that large scale production would place on an individual region's resources.

Bibliography:

American Oil Chemists' Society. Official Methods and Recommended Practices. 4ed. Champaign AOCS. 2v. 1990

Balslev, H. and Moraes, M. Sinopsis de las palmeras de Bolivia. AAU reports 20. Botanical institute Aarhus university, 1989.

Berger, K. G. and, Ong, S.H. The Industrial Uses of Palm and Coconut Oils. Oléagineux v.40 p. 613-621. 1985.

Blicher-Methiesen, U., and Balslev, H. *Attalea colenda* (Arecaceae), a Potential New Lauric Oil Resource. Economic Botany v. 44 p. 360-368. 1990.

Boom, B. M. The Chácobos indians and their palms. In The Palm - Tree of Life: Biology, Utilization and Conservation. Balick, M. J. (ed.). Advances in Economic Botany 6: 91-97. 1988.

Calais, P., and Clark, AR. Waste Vegetable Oil As A Diesel Replacement Fuel. Western Australian Renewable Fuels Association Inc. 1999.

Cardenas, M. Manual de plantas economicas de Bolivia, 2a. ed. Editorial Los Amigos del Libro, La Paz-Cochabamba, p.399. 1989.

Cole, A.R.H, Watts, D.W. & Bucat, R.B. Chemical Properties and Reactions University of Western Australia Press, Perth, 1978.

Corrêa, Pio, M. Dicionário das plantas úteis do Brasil e das exóticas cultivadas. 2. ed. Ministério da Agricultura, Instituto Brasileiro de Desenvolvimento Florestal, Rio de Janeiro: v. 8, p.486 1984.

Deffeyes, K. Hubbert's Peak. The Impending World Oil Storage. Princeton University Press. 2001.

Dukes, J., Burning Buried Sunshine: Human Consumption of Ancient Solar Energy. Climatic Change, v.61, p.31-44, 2003.

Ferreira, E. J. L. . personal communication. August, 2004. "Manual de palmeras do Acre" (in preparation).

Galeano, G. G. & R. Galeano Bernal. Palmas del Departamento de Antioquia-Región Occidental. Universidad Nacional de Colômbia, Centro Editorial, Bogotá, p.221. 1987.

Hilditch, T.P., and Williams, P.N. The Chemical Constitution of Natural Fats, 4th Edition. Chapman and Hall, London. 1964.

Howell, S., and Weber, A., Biodiesel Use in Underground Metal and Non-metal Mines. DieselNet Technical Report, www.DieselNet.com, May 1997.

Hunt, J., Petroleum Geochemistry and Geology, W.H. Freeman and Company, San Francisco, CA, 1979.

Instituto Adolfo Lutz. Normas Analíticas do Instituto Adolfo Lutz: Métodos Químicos e Físicos para Análise de Alimentos. São Paulo. 3ª ed, v.1, 1985.

Lleras, E. and Coradin, L. Native Neotropical Oil Palms: State of the Art and Perspectives for Latin America. Advances in Economic Botany. v.6 p.201-2013. 1988.

Mackenzie, F. T., Our Changing Planet: An Introduction to Earth System Science and Global Environmental Change, Third Edition, Pearson Education, Inc., Upper Saddle River, New Jersey, 2003.

Mejia, C. K. Utilization of palms in eleven mestizo villages of the Peruvian Amazon (ucayali river, departament of loreto). Advances in Economic Botany 6: 130-136. 1988.

Moraes, M., Borchsenius, F., and Blicher-Mathiesen, U. Notes on the Biology and Uses of the Motacú Palm (Attalea phalerata, Arecaceae) From Bolivia. Economic Botany, v50, p.423-428. 1996.

Munack, A., Shroder, O., Krahl, J., and Bunger, J., Comparison of Relevant Exaust Gas Emissions from Biodiesel and Fossil Fuel. CIGR eJournal v.3, 2001.

Nauss, K., Diesel Exaust: A Critical Analysis of Emissions, Exposure, and Health Effects. DieselNet Technical Report, www.DieselNet.com, October 1997.

Pesce, C. Oleaginosas da Amazonia. Oficinas Gráficas da Revista da Veterinaria 1941. Translated and Edited by Dennis V. Johnson. Reference Publications Inc., Algonac, Michigan. 1985.

Sheehan, J., Comobreco, V., Duffield, J., Graboski, M., and Shapouri, H.. An Overview of Biodiesel and the Petroleum Diesel Life Cycles. NREL, May 1998.

Sheehan, J., Dunahay, T., Benemann, J., and Roessler, P., A Look Back at the U.S. department of Energy's Aquatic Species Program: Biodiesel from Algae. NREL, July 1998.

Schlesinger, W., Biogeochemistry: An Analysis of Global Change, Second Edition, Academic Press (USA), San Diego CA, 1991.

Tickell, J.. From The Fryer to the Fuel Tank: The Complete Guide to Using Vegetable Oil as an Alternative Fuel, Third Edition, edited by Kaia Roman, publ. Tickell Energy Consultants, Covington LA, 2003.

Tissot, B.P., and Welte, D.H., Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration, Springer-Verlag, Berlin Heidelberg, New York, 1978.