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BIODIESEL PRODUCTION OPTIMIZATION AND QUALITY ASSESSMENT USING JATROPHA CURCAS OIL AND ETHANOL ALCOHOL

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BY

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This work is dedicated to my co-adviser Muluken Getnet. RIP

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Table of Contents

Pages

List of Table

List of Figures

ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
AV	Acid Value
CJCO	Crude Jatropha Curcas Oil
CSTR	Continuously Fed Stirred Tank Reactor
EPE	Ethiopian Petroleum Enterprise
FDRE	Federal Democratic Republic of Ethiopia
FFA	Free Fatty Acid
GHG	Green House Gas
HFO	Heavy Fuel Oil
JCL	Jatropha Curcas Linnaeus
JCO	Jatropha Curcas Oil
JOEE	Jatropha Oil Ethyl Ester
LFO	Light Fuel Oil
LPG	Liquid Petroleum Gas
MeOH	Methoxide
MI	Mixing Intensity
MR	Molar Ratio
MT	Metric tone
NA	Not Available
NaOH	Sodium Hydroxide
RT	Reaction Time
SVO	Straight Vegetable Oil
US	United States
USD	United States Dollar

ABSTRACT

Concern over high transportation fuel costs, trade deficits, depleting resources, energy security, and mounting evidence of global climate change has led to re-investigation of fossil fuel alternatives. For this reason Ethiopian Ministry of Water and Energy has started promoting bio-energy as a means to transform the nation’s abundant renewable biomass resources into cost competitive, high power biofuels and products. Biodiesel offers one renewable fuel option that can be produced from non edible vegetable oil sources. Fortunately Ethiopia has many opportunities for biodiesel production. The country´s favorable climatic condition for the cultivation of non edible vegetable oil bearing plants and the abundance of ethanol alcohol produced from the byproduct of local sugar factories gave the country a great advantage in producing biodiesel and get a little relief from petroleum related problems. However, the effort made to introduce the technology and take the most out of it is so low to force policy makers and encourage local and foreign businessmen towards the production of biodiesel using local resources. Therefore this research tries to fill this gap.

The main purpose of this research is therefore to develop a biodiesel production technique from Jatropha oil (Jatropha curcas Linnaeus) and a locally produced ethanol alcohol. Special attention was paid to the optimization of base-catalyzed transesterification for converting fatty acid ethyl ester (FAEE). The crude Jatropha oil used in the transesterification contained 5.01 mg KOH/g of acid and after neutralization it was possible to bring down the acid value to 1.35 mg KOH/g. Inorder to determine the optimum condition for tranestefication of Jatopha oil using ethanol and caustic soda as input, 16 experiments varyings ethanol-to-oil molar ratio (6:-9:1) and reaction temperature (55, 65, 70, and 78 ^{o}C). Reaction time, mixing intensity, and catalyst concentration was fixed to 3 hrs, 600 rpm, and 1.5 % by weight of the oil respectively.

The optimum conditions found for transesterification were an ethanol-to-oil molar ratio of 9:1 and a reaction temperature of 70 ^{0}C. At the optimum condition obtained a FAEE conversion of 80 % v/v was achieved. The resulting Jatropha biodiesel has, a density of 0.86 g/ml, viscosity of 4.13 mm^{2}/s, acid value of 0.71 mg KOH/g, and flash point of 173 ^{0}C satisfing ASTM D6751-02 and EN 14214 biodiesel standards. The production proces developed in this work will be used in production of a small scale plant withh capcity of 300 liter per day.

CHAPTER 1

1. INTRODUCTION

1.1 Background and Justification

The worlds' energy demand is escalating exponentially due to the rise in population and income. The escalated demand along with depletion of existing resources is fueling the escalation of fuel price. Beside the ever growing price of petroleum, the world is also anguishing from its emission related problems such as global warming, ozone layer depletion and the consequence of climate change: drought, and flooding.

Ethiopia, imports its entire petroleum fuel requirement and the demand for petroleum fuel is rising rapidly due to a growing economy and expanding infrastructure. The annual consumption of petroleum fuels amounts to more than 1.2[a] million tones which is equivalent to 5.4% of total final energy consumption. Imported petroleum products accounts about 40% of the total imports and absorbs 60% of export earnings.

These and other related problems are forcing the country to find some other alternative fuel that can substitute petroleum and helps to mitigate the consequential problems related with petroleum. Among the alternatives, Biodiesel which can be produced from non-edible oil like Jatropha is the best solution. Its production from Jatropha becomes a worldwide issue for its multi dimensional advantage including its drought–resistant, growing ability in marginal/poor soil, and its yielding ability for about 50 years. Moreover this wonder plant produces seeds with oil content 34% by weight and its oil can be combusted without being refined [37]. The by-product is also a good fertilizer.

[b]In Ethiopia the gross available potential land for production of feedstock for biodiesel is estimated about 23.3 million hectares. Regionally, the available land in million ha is: Oromia 17.2, Benishangul-Gumuz 3.1, Gambela 2.8, Somali 1.5, Amhara 1, Southern Nation Nationalities 0.05, and Tigray 0.007.

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[a] Source: Ethiopian Petroleum Enterprise Report, 2011

[b] Source: FDRE Ministry of Mines and Energy "The Biofuel Development & Utilization Strategy", Aug 2007

Consequently Ethiopian government has developed a strategy based on the assumption that Jatropha Curcas as a principal feed stock for biodiesel production. Even though the country possesses such an opportunity, practical action are not taken to produce the oil and make it available to the local consumption. Rather there are more than 50 developers registered only involved in plantation of energy crops mainly Jatropha and Castor.

This research, therefore, is intended to fill this gap by setting up a technical insight towards a small scale biodiesel production from jatropha curcas. Small scale production of biodiesel consists of three steps such as oil extraction, oil purification, and processing of oil. Oil extraction from jatropha seeds can be done by three different methods. These are mechanical extraction using a screw press, solvent extraction and intermittent pres extraction techniques. The selection of the extraction method will be subjected to availability, coast, quality, etc. The purification will be carried out by boiling the oil with water. After the oil is purified it will be directed to the third step. This step is the final step in processing the vegetable oil into diesel oil. In this process the oil will be transesterified using base catalysts like potassium hydroxide/sodium hydroxide and ethanol. Ethanol is preferred here since it is available at a local market. After the transesterification process biodiesel fraction of the oil is then washed and dried.

Quality assessment of the biodiesel is then will be performed for the three phases of production namely pre-production, production, and post-production phases. In the pre-production phase the physical property and quality of the feed stock will be assessed. In the production phase, the production process quality will be assessed based on the procedure given by ASTM and EN stanadards. In final phase, which is the post-production quality of the produced biodiesel will be assessed taking storage condition as a main variable. This assessment will be conducted taking the ASTM 6751-02 for biodiesel as a bench mark.

1.2 Objectives

The general objective of this thesis is to find the best way of optimizing the production system of biodiesel from jatropha curcas oil and a locally produced ethanol alcohol and catalayst (NaOH).

Specific objectives of this research are:

- Acquisition of biodiesel production process
- Pilot plant design of small scale biodiesel production plant
- Biodiesel production optimization from jatropha curcas oil (JCO) using ethanol alcohol and sodium hydroxide catalyst
  - Optimization of ethanol content and
  - Reaction temperature for the transesterification process
- Quality assessment for the biodiesel production system
  - Pre-production quality
  - Post-production quality

1.3 Thesis Organization

This thesis is divided into five chapters. Following this chapter, the second chapter, Review of Literature, deals with the literature review and past work done in this area. The third chapter, Materials and Method, involves description of the materials and their design used to solve the given problem. More over it deals with the lab scale biodiesel production procedure. Besides it lists the assumptions made during the entire.

The fourth chapter, Results and Discussions, describe the results that were obtained and discuss why those results are obtained. The fifth chapter, Conclusions and Recommendation, describes the conclusion made from the results obtained and points out some points recommended for future work that is possible in this area.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Overview of Small Scale Biodiesel Production and Quality Assessment

Because of concern for the the environmental degradation and the escalation of fuel prices of fossil-fuels, developing alternative resources of energy as a substitute for traditional fossil fuels has been risen. Biodiesel is among those alternatives that can prtially replace fossil fuels. Biodiesel in short is defined as alternative fuel for diesel engines produced by chemical reaction of a vegetable oil or animal fat with an alcohol such as ethanol [31, 32].

Straight vegetable oils (SVO) were proposed as diesel fuels as they are widely available from a variety of sources and they are renewable [2, 50]. However, they were found to be problematic due to their higher viscosity which affects the piston of injection pump and cause carbon deposits on piston and the cylinder head [2, 62]. Conversion of the oils to their alkyl esters reduces the viscosity to near the diesel fuel levels and produced a fuel with properties that is similar to petroleum based diesel fuel which can be used in existing engines without modifications. The main advantages of using biodiesel fuels as 100 % methyl or ethyl esters of vegetable oil and animal fat or biodiesel blends (up to 20 % blend to the diesel fuel) are producing less smoke and particulate matter, results in higher cetane numbers that makes combustion smooth and produces lower carbon monoxide and hydrocarbon emissions [30].

2.2 Feedstocks Development for Biodiesel Production

Biodiesel can be produced from a great variety of feedstocks. These feedstocks include most common vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils) and in recent publications microbial algae is also declared as a third generation feed stock [77]. Many researchers have reported on the use of different vegetable oils to produce biodiesel. Several researchers [25, 35, 61, 70, 75] used jatropha oil to produce a biodiesel that satisfy the ASTM standards. On the other hand other reseachers studied the parameters affecting the transesterification process of castor oil [46] and tested the performance of an internal combustion engine using a biodiesel derived from castor bean oil [4]. Similar works were done on transesterification of soybean oil and beef tallow [15, 22, 27].

From these research works it is clear to understand that there are a wide variety of feed stocks but the choice depends on local availability, affordability and government incentives. For example, rapeseed oil is preferred in Western Europe, while the United States favors refined soybean oil as a feedstock [50]. Although Brazil is the world‘s second-largest producer of soybeans, its government is fostering a castor oil–based biodiesel industry. On the other hand jatropha curcas is the primary feed stock in India and China [13].

2.3 Status of Biodiesel Production: World Vs Ethiopia

World

The global market for biodiesel is showing an increasing growth rate for the last ten years. Biodiesel has shown an average annual energy growth rate of 41.2%tfrom 2000 to 2008 which is the highest growth rate compared with other energy sources. As Fig 2-1 shows the world biodiesel production has escalated from 916.8 millions of liters in 2000 to more than 17.8×10^3 millions L in 2009. The consumption is also growing from year to year as shown in Fig 2-2. This increase in growth rate is due to its correlation with sustainable development, energy conservation, management, efficiency and environmental preservation.

It is expected that Biodiesel could represent as much as 20% of all on-road diesel used in Brazil, Europe, China and India by the year 2020 [6]. Rapid growth in biodiesel demand in the EU, USA and Asia is driving investment in the global trade of alternative feedstocks. In terms of the market size, the biodiesel industry has reached more than 17.8×10^3 millions gal in 2009, with Europe having the largest share of the market (the market share for Europe has reached 56% in 2009[a]) [13].

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[a] *Source: US Energy Information Administration Independent Statistics and Analysis*

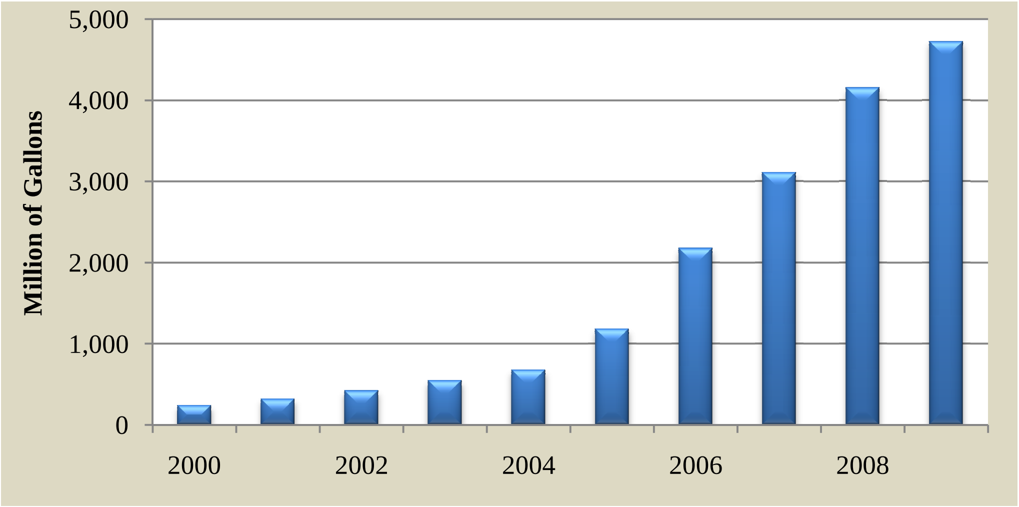

Fig 2-1 World biodiesel production from 2000-2009

Source: US Energy Information Administration Independent Statistics and Analysis.

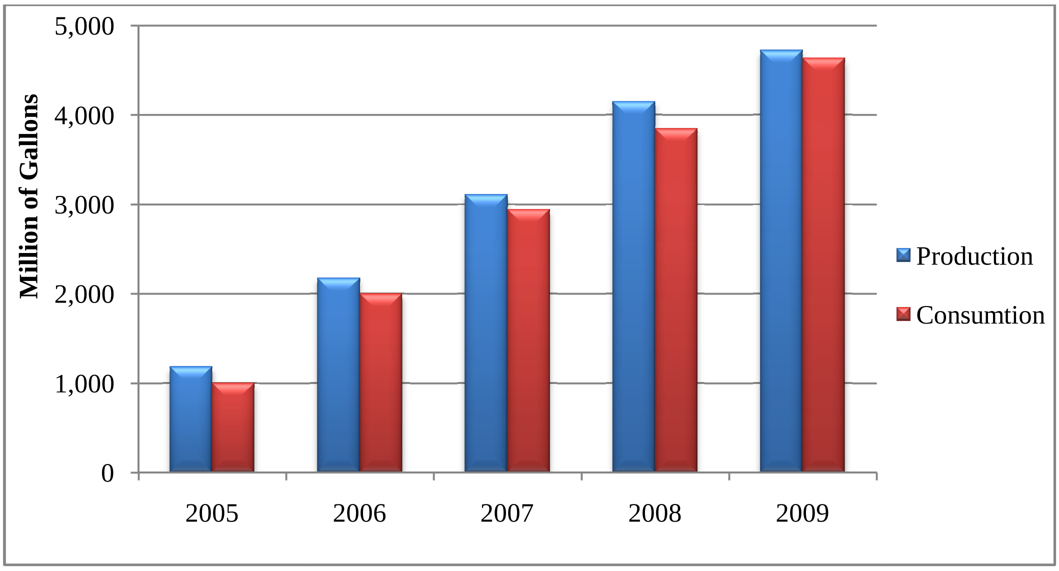

Fig 2-2 World biodiesel Production Vs Consumption

Source: US Energy Information Administration Independent Statistics and Analysis.

Ethiopia

Ethiopia, as most of non petroleum producing countries, is entirely dependent on imported products of petroleum., Gasoil, Gasoline, Jet/Kerosene, fuel oil and LPG are the main imported products of petroleum. Form these products gasoil/diesel oil takes the major part from the imported product. The report organized by EPE (Fig 2-3) reveals that the demand for gasoil has doubled within a decade. Moreover the per-metric ton price has also increased by three fold in ten years. This shows clearly that how the economy of the country is affected by the imported of petroleum products.

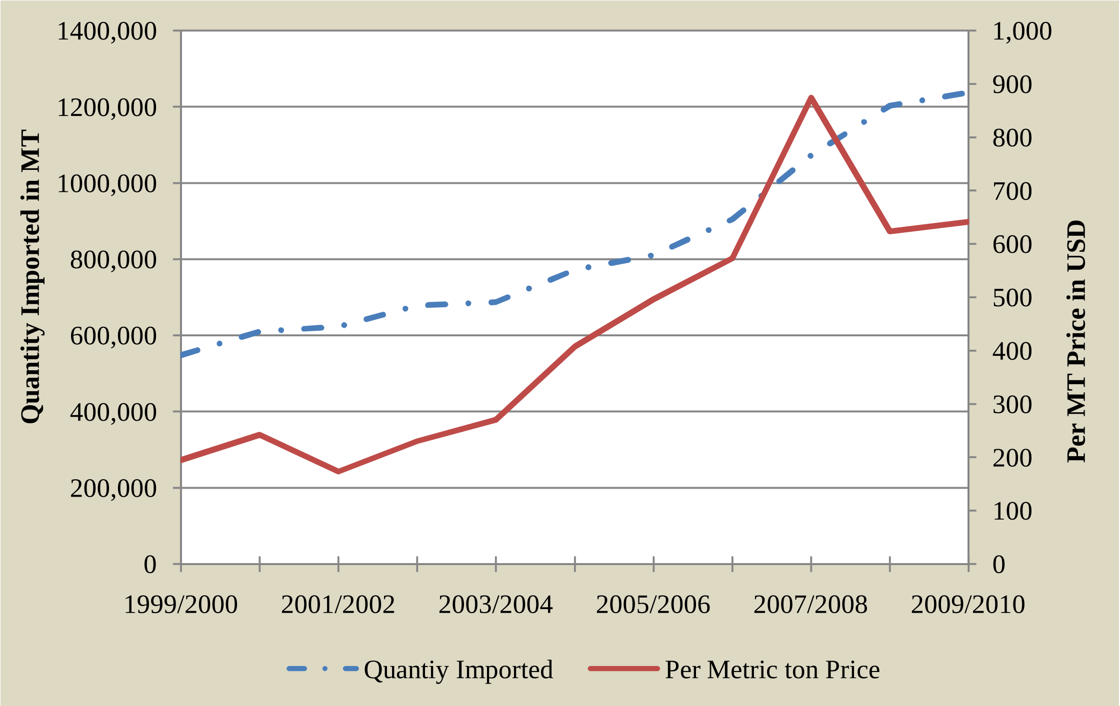

Fig 2-3 Ethiopian Gasoil Import Status from 1999-2010

Source: Ethiopian Petroleum Enterprise

Therefore to speed up the development of the country by improving export-import trade balance, the imported quantity or the per-metric price should be curtailed. Since the later is impractical, the only option is to minimize the imported quantity and compensate the deficient with appropriate substitute such as Biodiesel that can be produced locally. For this reason the FDRE ministry of Energy and Water has formulated "The Biofuel Development & Utilization Strategy" to facilitate adequate production of biofuels from indigenous resources. According to the strategy the biodiesel that is to be produced from ***jatropha curcas, caster bean***, and ***palm tree*** aimed to

- Ensure use of biodiesel for transportation
- Ensure a high level of blend
- Substitute biodiesel for domestic cooking and lighting fuel, etc

Based on this strategy local and foreign private investors have started growing plants for producing biodiesel. Until recently, the progress shows that over 14 private investors[a] are undertaking preparations for the production. However, not a single company reported to start the biodiesel production yet! More rececently, its is stated to subsistitute 5%[b] of diesel fuel by Jatropha in the Green development startegy of the country.

2.4 Jatropha Curcas Linnaeus: The Renewable Energy Plant

2.4.1 Name and Plant Description:

The genus *Jatropha* belongs to tribe *Joannesieae* of *Crotonoideae* in the *Euphorbiaceae* family and contains approximately 170 known species [26**]**. The genus name *Jatropha* derives from the Greek word *jatrós* (doctor) and *trophé* (food), which implies medicinal uses. *Curcas* is the common name for physic nut in Malabar, India [47]. The father of modern taxonomy, the Swedish botanist Carl Linnaeus, was the first to name the physic nut *Jatropha curcas in 1753* [68] according to the binomial nomenclature of “Species Plantarum.” Scientists Bijan Dehgan and Grady Webster have postulated that *Jatropha curcas* is the most primitive form of the *Jatropha* genus. Some research works stated that this plant was originated from the Caribbean, where the species was already been used by the Mayas, was most likely distributed by Portuguese ship via the Cape Verde Island and Guinea Bissau to other countries in Africa and Asia [68].

It is a small tree or large shrub, which can grows between 3 to 5 meters in height, but can attain a height up to 8 to 10 m in favorable conditions. The branches contain latex, roots are formed from seeds, one central (tap root) and four peripheral. Cuttings, when planted do not form tap root. The plant is monocious and flowers are unisexual. Pollination is by insects. The life span of the plant is more than 50 years [47].

2.4.2 Potential Uses of Jatropha curcas L

It is reported that Jatropha is planted as a hedge or living fence by farmers all over the world around homesteads, gardens and fields, because it is not browsed by animals [36].

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[a] Ethioipian Petroluem Enterprise Report, 2011

[b] Source: FDRE Ministry of Mines and Energy “The Biofuel Development & Utilization Strategy”, Aug 2007

The root, stem, leaves, fruit, seed, bark and latex of the plant are largely used for many medicinal purposes in different parts of world. The flowers also attract bees and thus the plant has a honey production potential [10].

Hedge

Jatropha is an excellent hedging plant in fields and settlements. This is mainly because it can easily be propagated by cuttings and because the species is not browsed by cattle. It is one of the hedge plants mostly found in different parts of the world such as, El Salvador, Upper Guinea, Mali, India, Zambia [36, 47, 38], Ethiopia [28], etc.

Fig 2-4 Jatropha hedge around a homestead

Medicine

All parts of the plant, including seeds, leaves and bark, are used in traditional medicine especially for veterinary purposes [10, 36]. Since the seed oil has purgative action it is widely used to heal eczema and skin diseases and to soothe pain that is caused by rheumatism. A decocted leaves is also used against cough and as a disinfectant after birth [36]. A decoction of the root is reported to treat diarrhea and gonorrhea [68]. The latex that is extracted from the stem has been used for healing wounds and stopping bleeding. [36, 68].

Fertilizers

Since the seed cake is highly rich in nitrogen, it is an excellent source of plant nutrients. Some research reported that in a green manure trial with rice in Nepal, an application of 10 tons of fresh jatropha biomass gives an increase yield of many crops [72]. As a straight fertilizer, its nutrients were compared with those of other organic fertilizers with regard to nitrogen, phosphorus and potassium content which is shown in the Table 2-1.

Table 2-1 Nutritional analysis of Jatropha oil seed cakes, and manure (%) [a]

Nutrients	J. Curcas oil cake[b]	Neem Oil cake	Cow manure
Nitrogen	6	5.0	0.97
Phosphorus	3	1.0	0.69
Potassium	1	1.5	1.66

Pesticide

Extract from all parts of the jatropha plant shows insecticidal properties. The seed oil, extracts of physic nut seeds and phorbol esters from the oil were used to control various pests with, in many cases, successful result. In general the aqueous extract of jatropha seed and leaves were proved effective in controlling insects of pests of cotton, corn, sorghum, and potato [36].

Erosion control and improved water infiltration

Jatropha has proven effective in reducing erosion of soil by rainwater. The taproot anchors the plant in the ground while the profusion of lateral and adventitious roots near the surface binds the soil and keeps it from being washed out by heavy rains. Jatropha also improves rainwater infiltration when planted in lines to form contour bunds [68].

Soap

The glycerin which is a by-product of biodiesel can be used to make soap, and soap can be produced from *Jatropha* oil itself. In either case the process produces a soft, durable

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[a] *Source:* Ashwani Kumar et. al. ¨Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines¨, 2006

[b] *Source: Chinmoy Baroi et al. ¨ Biodiesel Production from Jatropha curcas Oil Using Potassium Carbonate as an Unsupported Catalyst¨, 2009*

soap and is a simple one, well adapted to household or small-scale industrial activity [10, 14, 25, 41].

Fig 2-5 Soap Produced from Jatropha Oil

Food

Though jatropha seed is toxic when consumed, non-toxic variety of jatropha is reported to exist in some province of Mexico and Central America which do not contain phorbol ester [10, 14, 36]. José Angel Sotolongol et al.(2003), reported that jatropha seed is eaten in certain region of Mexico (in the region of Misantla, Veracruz, there is a non toxic variety) once it is boiled and roasted.

Energy Ssource

The oil from *Jatropha* is regarded as a potential fuel substitute. The types of fuels, which can be obtained directly from the *Jatropha* plant, are; wood, the whole fruit and parts of the fruit which can be burnt separately or in combination [2, 42, 75].

2.4.3 Yield of Jatropha

Jatropha trees are said to begin producing a measurable amount of nuts at 18 months, but are not expected to reach maturity and optimal yields until after 6 years. Seed yield in jatropha curcas varies widely, which is logical for a plant that can grow in different conditions. Conditions such as spacing between plants, climatic condition, soil status (ranging from marginal to fertile, and if fertilizer was applied), age of the plants, and water feed systems (whether it is rain feed or irrigated) are the major conditions that can influence the yield of the plant. For example a widely spaced plant can yield more than a closely spaced since there will be a less competition of moisture and nutrients.

Similarly an irrigated plant will yield continuously throughout the year whereas a rain feed plant will give only seasonally.

Recent publications reported that seed yield varies from 0.2 to more than 2 kg / plant / year depending on the age of plant and soil/climatic conditions [47, 65, 68].

On an area basis, Richard Brittaine et al.(2010), by citing [58] reported seed yields between 0.4 to 12 tons/ha, [67] reported a productivity of the plant varying from 1.5 to 6 tons/ha/year, and [36] reports another yield range between 0.1 and 8.0 tons/ha. Larger range of yield from 0.1 to 15 tons/ha/yr is also reported by [10]. This kind of discrepancy in yields of jatropha plant is originated due to over projection based on the yield of single tree or few trees. For example, a vigorously growing six-year old Jatropha tree growing on a farm produced more than 3.0 kg of seed. It will be unrealistic, however, if the per ha seed production is estimated based on the unusually high seed yield of this single tree [23]. Moreover, these yield figures are accompanied by little or no information on genetic provenance, age, propagation method, pruning, rainfall, tree spacing, soil type or soil fertility, and location of plantation.

Since climatic condition and soil status are the major factor in influencing the yield of jatropha, I will brief a little on these issues as follows.

Table 2-2 Jatropha Curcas L. seed yield

Country	Seed yield	Plant Spacing	Plant Age	Reference
Mali	2800 kg/yr/ha	Not Specified	Not Specified	[37]
Nicaragua	5000 kg/yr/ha	Not Specified	Not Specified	
	2500 kg/ha/yr	Not Specified	after 4 years	[9]
Brazil	335 kg/ha	4x3m; 833 pl/ ha	after 12 months	[65]
	190 kg / ha	8x2m; 625 pl/ ha	after 9 months	
	56 kg/ha	8x2m; 625 pl/ ha	after 7 months	
India	600 kg/ha	833 pl/ha	after 2.5 years	[a][65]
	1450 kg/ha	1667 pl/ha	after 2.5 years	
	4000 kg/ha/yr	Not Specified	after 5 years	[9]
	2000 kg/ha/yr	Not Specified	after 3 years	

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[a] Experimental results on marginal soil

2.4.4 Favorable Climate and Soil Condition

Jatropha grows in tropical and sub tropical regions, with cultivation limits at 30^0 N and 35^0 S (refer [a]Fig 2-6). It also grows in lower altitudes of 0-500 meters above sea level [36]. While jatropha can survive with as little as 250 to 300 mm of annual rainfall, at least 600 mm are needed to flower and set fruit. The optimum rainfall for seed production is considered between 1000 and 1500 mm [9].

Jatropha showed, as reported by [9], significant occurrence for Annual Mean Temperature between 18 and 29 ^{0}C, with optimal values of 26–27 ^{0}C. Very high temperatures can depress yields. Jatropha has been seen to be intolerant of frost.

The best soils for jatropha are aerated sands and loams of at least 45 cm depth [36]. Heavy clay soils are less suitable and should be avoided, particularly where drainage is impaired, as jatropha is intolerant of waterlogged conditions. Ability to grow in alkaline soils has been widely reported, but the soil pH should be within 6.0 to 8.5. Jatropha is known for its ability to survive in very poor dry soils in conditions considered marginal for agriculture, and can even root into rock crevices. However, survival ability does not mean that high productivity can be obtained from jatropha under marginal agricultural environments. Being a perennial plant in seasonally dry climates, soil health management under jatropha production would benefit from conservation agriculture practices. This would result in minimum soil disturbance, an organic mulch cover on the soil surface and legume cover crops as intercrops.

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[a] *Source: Richard Brittaine et. al. ¨Jatropha: A Smallholder Bioenergy Crop The Potential for Pro-Poor Development¨, 2010*

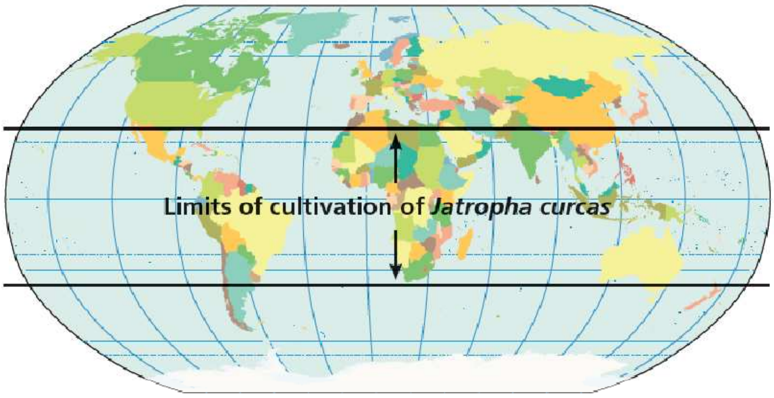

Fig 2-6 Jatropha Belt (30º N, 35º S)

2.4.5 *Composition of Jatropha Seed*

The fruit of J. curcas contains mostly three seeds. The seeds make up about 70% of the total weight of the fruit (30% fruit coat) [58, 65]; the mature fruits have a moisture content of about 15%, the seeds about 7%. The oil is stored in the interior of the seed: the kernel, which makes up about 65% [1] of the total mass of the seed. The moisture contents are about 10% for the hull and 3-11% [36, 73] for the kernel. Lots of previous works have been done by different scholars so as to determine oil content of jatropha seed. As Table 2-3 shows there is a wide range in oil content and this is possibly due to the variation in plantation condition and/or oil extraction method.

The seed of JCL is about 6.6% water, 18.2% protein, 38% oil, 17.2% carbohydrates, 15.5% fiber, and 4.5% ash by weight of seed [45]. Here, the amount of actual oil produced from seeds and kernels is contingent upon different conditions such as plantation condition and mostly the method of extraction. For example with hand presses extruding only about 20% and more sophisticated a much higher quantity can be obtained [14].

When it comes to the fatty acid compositions there are three main types of fatty acids that can be present in a triglyceride of Jatropha; which are saturated (Cn:0), monounsaturated (Cn:1) and polyunsaturated with two or three double bonds (Cn:2,3) [10]. Though various vegetable oils are potential feedstocks for the production of a biodiesel, the quality of the fuel will be affected by the oil composition. Ideally the vegetable oil should have low saturation and low polyunsaturation i.e. be high in monounsaturated fatty acid [25].

Table 2-3 Oil content of Jatropha Curcas L

Fruit part	**Oil content (%)**	**Reference**
Seed	33.6-37	[65]
	33-39.1	[34]
	37.4	[48]
	38	[45]
	35-40	[14]
	40	[10]
	30-50	[5]
	45-60	
Kernel	55-60	[14]
	46.2-58.1	[34]
	46.0-48.6	[48]
	21-74	[71]
	63.16	[25]
	66.4	[1]

Based on this fact jatropha seed oil has an advantage over other vegetable oils such as palm oil, sunflower oil and soybean oil for possessing a highest monounsaturated/Oliec acid. Here also (refer Table 2-4) different figures of fatty acid compositions have been reported in different works. The reason for this lack of similarity in fatyy acids composition is the same as the oil content. But it requires a thorough research to investigate the exact reason.

Table 2-4 Fatty acid composition of seed oil of jatropha curcas L

Fatty acid	**References**				
	[36]	[a][41]	[62]	[25]	[47]
Myristic acid (C14:0)	NA	0.15	0.1	0.1	0.38
Palmitic acid (C16:0)	15.38	12.3	15.1	14.2	16.0
Palmitoleic acid (C16:1)	NA	0.55	0.9	0.7	1-3.5
Stearic acid (C18:0)	6.24	2.8	7.1	7.0	6-8
Oleic acid (C18:1)	40.23	47.1	44.7	44.7	42-43.5
Linoleic acid (18:2)	36.32	36.7	31,4	32.8	33-34.5
Linolenic acid (18:3)	NA	0.18	0.2	0.2	0.8
Arachidic acid (20:0)	NA	NA	0.2	0.2	NA

2.5 Biodiesel Production

2.5.1 Vegetable Oil as a Fuel

The use of vegetable oils in diesel engines is nearly as old as the diesel engine itself. The inventor of the diesel engine, Rudolf Diesel, reportedly used groundnut (peanut) oil as a fuel for demonstration purposes [31]. Dr. Diesel in his book entitled “Liquid Fuels,” addresses the use of vegetable oils as a fuel: “For [the] sake of completeness it needs to be mentioned that already in the year 1900 plant oils were used successfully in a diesel engine. During the Paris Exposition in 1900, a small diesel engine was operated on ***peanut oil*** by the French Otto Company. It worked so well that only a few insiders knew about this inconspicuous circumstance. The engine was built for petroleum and was used for the plant oil without any change.” [50].

From the day of the Paris exposition the world has been using vegetable oil in diesel engines. In the 1930s and 1940s, vegetable oils were used as diesel substitutes as emergency fuels and for other purposes, especially during World War II [2, 50] In this

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[a] Sample specifically from Pueblillo (Papantla, Ver.) province, Mexico

period for example the Japanese battleship called *Yamato* reportedly used edible refined soybean oil as bunker fuel [50].

Even though vegetable oils are good substitutes of petroleum-diesel, due to their economical infeasibility the world has given his back for the issue. However, because of the increase in crude oil prices, limited resources of fossil oil and environmental concerns in recent days, there has been a renewed focus on vegetable oils in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soybean oil in the USA, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in Philippines are being considered as substitutes for mineral diesel [31].

There are still some problems that hinder the use of vegetable oil for substitute of petro-diesel. Vegetable oils have about 10% less heating value than diesel for the oxygen content in the molecule and the viscosity of vegetable oil is several times higher than that of mineral diesel due to large molecular weight and complex chemical structure. This high viscosity of vegetable oil, 35–60 mm^2/s compared to 4 mm^2/s for diesel at 40 ^0C [2], leads to problem in pumping and spray characteristics (atomization and penetration etc.). The inefficient mixing of oil with air contributes to incomplete combustion. High flash point attributes to its lower volatility characteristics. The combination of high viscosity, low volatility, and the polyunsaturated character of vegetable oils cause poor cold starting, misfire, ignition, high carbon deposit formation, injector coking, piston ring sticking and lubrication oil dilution and oil degradation [2, 62]. Because of these problems, vegetable oils must be chemically modified to a more suitable and compatible fuel for existing engines. This fuel modification is mainly aimed at reducing the viscosity to get rid of flow and combustion-related problems. This can be done in either of the following ways:

- Direct use and blending
- Micro-emulsion
- Pyrolysis (thermal cracking)
- Transesterification

Direct use and blending

Caterpillar (Brazil) in 1980 used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% mineral diesel was successful. Some short-term experiments used up to a 50/50 ratio. Pramanik, 2003, has found that 40 to 50% blend of Jatropha oil can be used in diesel engine without any major operational difficulties but further study is required for the long-term durability of the engine. Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines.

Micro-emulsion

A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures, formed spontaneously from two normally immiscible liquids. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been investigated in order to solve the problem of the high viscosity of vegetable oils. Short term performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of no.2 diesel, in spite of the lower cetane number and energy content. In a laboratory screening endurance test, however, irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscosity were reported [39].

Pyrolysis

Pyrolysis is the conversion of one substance into another by means of heat or by heat in presence of a catalyst. The payrolyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum [2]. Many researchers have studied the pyrolysis of triglycerides to obtain products suitable for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadines, aromatics and carboxylic acids. Soybean oil pyrolyzed distillate had a CN of 43, exceeding that of soybean oil (37.9) and the ASTM minimum value of 40. The viscosity of the distillate was 10.2 mm^2/s at 38°C, which is higher than the ASTM specification for DF2 (1.9-4.1 mm^2/s) but considerably below that of soybean oil (32.6 mm^2/s) [31]. Though pyrolyzed vegetable oils possess acceptable amounts of sulphur, water, and sediment, as well as giving acceptable copper corrosion values, they are unacceptable in terms of ash, carbon residues, and pour point. No matter how the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during thermal processing also eliminates any environmental benefits of using an oxygenated fuel [39].

Transesterification

Transesterification is the reaction of a fat or oil with an alcohol (in the presence of catalyst) to form esters and glycerol as a by-product [2, 39, 40]. Suitable alcohols include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently, because of their low cost and physical and chemical advantages [29]. The reactions are often catalyzed by an acid or a base, since the alcohol is sparingly soluble in the oil phase. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. The most common catalysts used are strong mineral bases such as sodium hydroxide and potassium hydroxide [43] but there are also some other catalysts used such as acid, enzymes and non-ionic base catalysts.. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance. Thus, fatty acid methyl esters (known as biodiesel fuel) obtained by transesterification can be used as an alternative fuel for diesel engines. Therefore the best way to use vegetable oil as a diesel fuel and overcoming the related problem is to convert it in to ***Biodiesel*** through a transesterification process. The details of the process of transesterification and biodiesel production are given as follows.

2.5.2 Biodiesel Production Process

Biodiesel is the name of a clean burning mono-alkyl ester-based oxygenated fuel made from natural, renewable sources such as vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut, jatropha) and animal fats (usually tallow) as well as waste oils (e.g., used frying oils) [50]. The resulting biodiesel is quite similar to conventional diesel in its main characteristics. Since biodiesel is miscible with petro-diesel in all ratios, in many countries, this has led to the use of blends of biodiesel with petrodiesel instead of neat biodiesel. The level of blending with petroleum diesel is referred as Bxx, where xx indicates the amount of biodiesel in the blend (i.e. B20 blend is 20% biodiesel and 80% diesel). The biodiesel production is comprises of two main sub processes namely oil extraction & purification and Transesterification processes. The details of the processes are discussed here after.

a) Oil Extraction and Purification

Oil Extraction

The ripe fruits are plucked from the trees and should be free from sand and dust. To prepare the seeds for oil extraction, they should be heated, either in full sunlight on a black plastic sheet for several hours or in a roasting pan for 10 minutes. The seeds should be heated, but not burnt. This process breaks down the cells that contain the oil, allowing the oil to flow out more easily. The heat also liquefies the oil, which improves the extraction process.

After the seed is prepared, it will be possible to carry on the extraction process. The extraction can be done by three different methods. These are mechanical extraction using a screw press, solvent extraction and intermittent pres extraction techniques. The oil yield varies depending on the extraction technique. With mechanical oil expellers, for example, up to 75 - 80 % of the oil can be extracted. Whereas with a hand press like the Bielenberg ram press like the one shown in Fig 2-1 only 60 - 65 % of the oil can be extracted (5 kg of seeds give about 1 liter of oil) [37].

Oil Purification

The oil extracted from the seed can be purified by the following means:

- **Sedimentation:** This is the easiest way to get clear oil, but it takes about a week until the sediment is reduced to 20-25% of the raw oil volume.
- **Boiling with water:** The purification process can be accelerated tremendously by boiling the oil with about 20% of water. The boiling should continue until the water has completely evaporated (no bubbles of water vapor anymore). After a few hours the oil then becomes clear.
- **Filtration:** Filtration of raw oil is a very slow process and has no advantage in respect of sedimentation. It is not recommended.

Fig 2-7 Bielenberg ram press for JCL seed

b) *Transesterification*

The transesterification reaction, explained in section 2.5.1, involves stepwise conversions of Triglyceride to Diglyceride to Monoglyceride to Glyceride producing 3 mol of ester in the process [29]. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Alkali-catalyzed transesterification is approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst transesterification. Partly for this reason and partly because alkaline catalysts are less corrosive to industrial equipment than acid catalysts, most commercial transesterifications are conducted with alkaline catalysts. Sodium alkoxides are among the most efficient catalysts used for this purpose [39, 29].

Kinetics of alkaline-catalyzed transesterification reactions

The transesterification reaction with alcohol represented by the general equation shown in Fig 2-8 consists of a number of consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, which is followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride at each step. The stoichiometry of transesterification reaction is as follows:

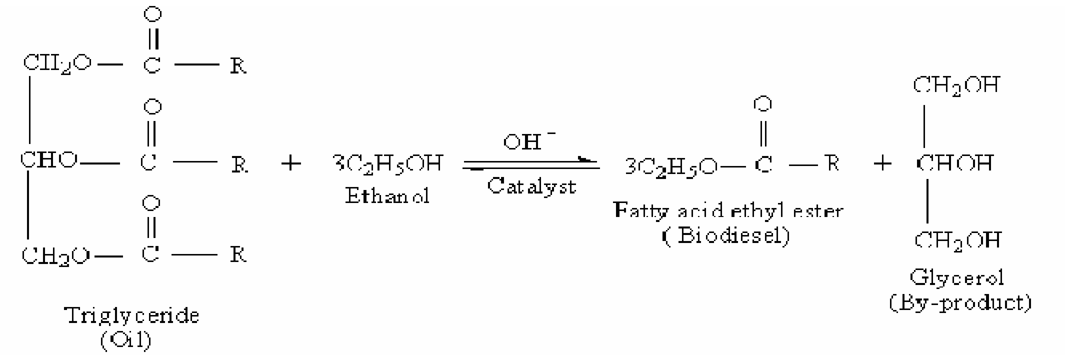


Fig 2-8 Stoichiometry of Transesterification of Triglyceride

Stepwise Reactions

1. $TG + ROH \underset{}{\overset{Catalyst}{\rightleftharpoons}} DG + R'CO2R$
2. $DG + ROH \underset{}{\overset{Catalyst}{\rightleftharpoons}} MG + R'CO2R$
3. $MG + ROH \underset{}{\overset{Catalyst}{\rightleftharpoons}} glycerol + R'CO2R$

Fig 2-9 Stepwise Reaction in Transesterification

2.5.3 *Transesterification Process Details*

Since transesterification is the major process in production of biodiesel I will concentrate on the details of the process as follows:

a) Oil Heating

In order to speed up the reaction as well as remove any water residue, the jatropha oil should be boiled at 105-110°C for at least 30 min [49, 54]. Heating should be stopped if there is no more water bubbles in the oil. When water is present, particularly at high temperatures, it can hydrolyze the triglycerides to diglycerides and form a free fatty acid [43]. It is important to stir the oil as it is heated. This will result in a more even heating and reduce the temperature of oil exposed directly to the heating element. After the entire water residue is removed from the oil it should be cooled to a temperature a little lower than boiling temperature of ethanol.

b) Mixing of Ethanol and NaOH

The purpose of mixing ethanol and the catalyst (NaOH) is to make the reaction for the two substances to form Ethoxide. Ethanol is preferred for two reasons; one for its abundance in local market and the other is for its capability for being renewable. It can be produced from agricultural renewable resources and from molasses, which is a byproduct of sugar industry.

c) Transesterification Reaction

In the transesterification reaction, the reactants initially form a two phase liquid system. Hence the reaction is diffusion controlled and poor diffusion between the phase results in a slow rate. Therefore in order to speed up the reaction between the mixture of Ethoxide and the oil, a mixing mechanism should be there. Experiment conducted by [51] reveals that transesterification of Jatropha curcas oil into butyl ester was function of mixing intensity. Best reaction rate in this experiment is observed for a rotational speed above 200 rpm. However this mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant and the reaction rate is primarily influenced by the reaction temperature. Many researchers [15, 22, 29] have conducted lots of experiment so as to find an optimum temperature. For an optimum yield of ethyl ester the reaction should be close enough to the boiling temperature of ethanol.

d) Draining of Glycerol

After the transesterification reaction, one must wait for the glycerol to settle to the bottom of the container. This happens because glycerol is heavier than biodiesel. The settling will begin immediately, but the mixture should be left a minimum of eight hours (preferably 12) to make sure all of the glycerol has settled out.

There will be a difference in viscosity and color between the two liquids. Glycerol looks very dark compared to the yellow biodiesel. The viscosity difference is large enough between the two liquids that the difference in flow from the drain can be seen.

e) Biodiesel Washing

The purpose is to wash out the remnants of the catalyst and other impurities. There are three main methods:

- Water wash only (a misting of water over the fuel, draining water off the bottom)
- Air bubble wash (slow bubbling of air through the fuel)

- Air/water bubble wash (with water in the bottom of the tank, bubbling air through water and then the fuel)

Which method works the best is dependent on the quality of the fuel. The mostly used method is a combination of water washing and air bubble washing. Warm water, usually from 49-60ºC [43], is misted above the fuel. The use of warm water prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. The amount of wash water should equal from 25-100% of the volume of oil [3, 19] and can be drained throughout the washing process.

After the water is drained, the air washing process can start. At this point, the biodiesel is usually a pale yellow color. Air should be bubbled through the biodiesel mixture for approximately 8 hours. The bubbling should be just enough to agitate the biodiesel surface. A final drain of accumulated contaminants is done immediately after the air bubble wash is finished. The fuel is now ready for use. During the washing process, gentle agitation is required to avoid the emulsion.

f) Biodiesel Drying

After the biodiesel is washed, it should be dried until it is crystal clear. This can be done by letting the biodiesel sit uncovered in a sunny location for a few days, or it may be heated to about 49 ^{0}C for a few hours. Another popular technique is recirculating the biodiesel from the bottom of the drying tank through a shower head or sprayer suspended above the top of the open tank. This increased contact with air will dry biodiesel in about an hour, depending on humidity. It should have a pH of close to 7, or chemically neutral and it should have no methanol left in it [19].

2.5.4 Variables Affecting the Yield of Transesterification

The yield of biodiesel in the process of transesterification is affected by several process parameters/variables. The most important variables affecting the yield of biodiesel from transesterification are:

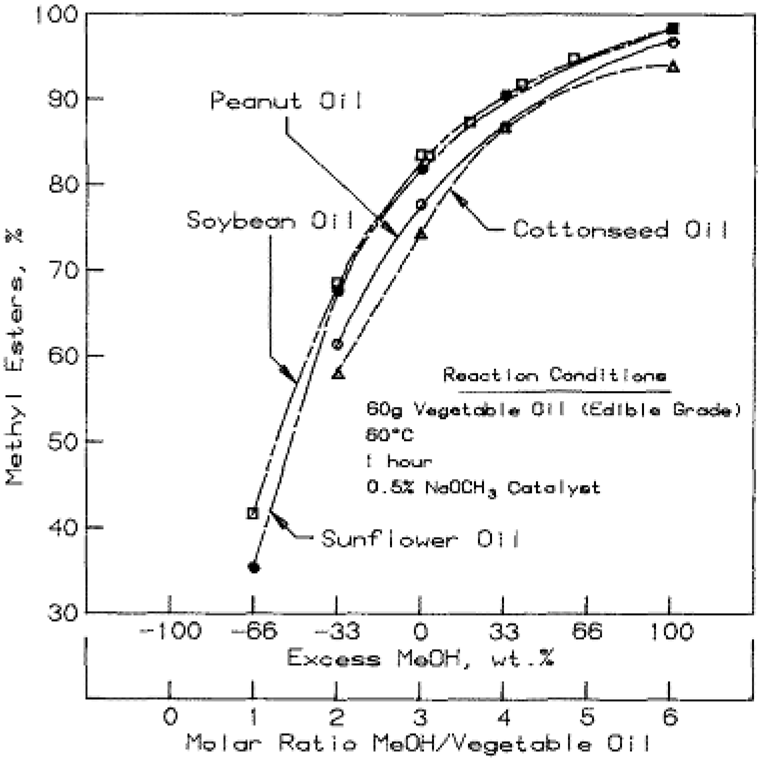
- ✓ Reaction temperature
- ✓ Molar ratio of alcohol and oil
- ✓ Catalyst concentration
- ✓ Reaction time
- ✓ Presence of moisture and free fatty acids (FFA)

a) Effect of Reaction Temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. The maximum yield of esters occurs at temperatures ranging from 60 to 80^{o}C at a molar ratio (alcohol to oil) of 6:1 [2, 53]. Generally, the reaction should be conducted close to the boiling point of the alcohol (in this case since the alcohol is ethanol, the temperature shouldn´t exceed 78^{o}C so as to not starve the reaction with ethanol) at atmospheric pressure for an optimum yield [29]. Several researchers have studied the effect of temperature on conversion of oils and fats into biodiesel. P. Nakpong et. al 2010 [60], studied the transesterification of jatropha curcas oil with methanol to oil ratio (6:1), 1% NaOH catalyst, at four different temperatures 60, 50, 40, and 32 ^{o}C. The results indicate that methanolysis could occur at room temperature (32°C), but it would be incomplete, even if the reaction time were extended to 40 minutes. For the same reaction time, the methyl ester content increased with temperature. The methanolysis proceeded to completion in 40 minutes at 60°C, yielding a methyl ester content of 98.6% w/w. Similar result is also reported by other researchers [29, 56]. The increase in the methyl ester content might have been due to the viscosity of the oil decreasing with an elevation of reaction temperature, which resulted in an increase in the solubility of the oil in the methanol, leading to an improvement in the contact between the oil and the methanol. Hence, the reaction was faster at a higher temperature. The same methyl ester content was achieved at a lower temperature as well, but the reaction time had to be increased. It shows that temperature clearly influenced the reaction rate and yield of esters and transesterification can proceed satisfactorily at ambient temperatures, if given enough time, in the case of alkaline catalyst.

b) Effect of Molar Ratio

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The Stoichiometry of the transesterification reaction requires 3 mol of alcohol per 1 mol of triglyceride to yield 3mol of fatty esters and 1 mol of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or remove one of the products from the reaction mixture continuously. The second option is preferred wherever feasible, since in this way, the reaction can be driven towards completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight. Freedman et al., 1984, studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93–98%) at a 6:1 molar ratio refer Fig 2-10. Ratios greater than 6:1 do not increase yield (already 98–99%), but it could shorten the reaction time. Experiment conducted by [60] has recorded a yield of 93.1% for a methanol-to-oil ratio of 8:1 and 10:1 after 10 and 5 minutes respectively. However, increasing the molar ratio beyond the 6:1 may interfere with separation of glycerol because there is an increase in glycerol solubility. When glycerin remains in solution, it will drive the equilibrium back to the left, lowering the yield of esters [62].



[a]Fig 2-10 Effect of Molar Ratio on Ester Formation

c) *Effect of Catalyst Concentration*

Partly due to faster esterification and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterification reactions are conducted with alkaline catalysts [2]. The alkaline catalyst concentrations

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[a] Adopted from Freedman B. et al. ´Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils´, 1984

in the range of 0.5–1% by weight yield 94–99% conversion of vegetable oils into esters [29]. Nakpong et al., 2010, studied methanolysis of Jatropha oil with NaOH catalyst. The result indicated that catalyst concentration of 1.5% w/w of oil provided a higher methyl ester content than that of 1% w/w of oil for all reaction times, but they suggested that such a concentration should be avoided for two significant reasons: the cost of the additional NaOH, and the cost of removing the residual catalyst in the methyl ester layer. Moreover, the methyl ester layer obtained from using this catalyst concentration has to be washed with hot distilled water several times in the water washing step, so there is a possibility of losing some biodiesel product to emulsion formation. For these reasons, 1% w/w of oil was considered to be the optimum catalyst concentration [60].

Sodium methoxide was found to be more effective than sodium hydroxide presumably because a small amount of water is produced upon mixing NaOH and MeOH [39, 40]. Sodium alkoxides are among the most efficient catalysts used for this purpose, though NaOH, due to its low cost, has attracted its wide use in large scale transesterification [2].

d) Effect of Reaction Time

The conversion rate increases with reaction time. Freedman et al., (1984), transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60 ^{o}C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93–98%). Investigation performed by [60] shows that at a reasonable alcohol to oil molar ratio and catalyst concentration a maximum yield is obtained after 40 minutes of reaction.

e) Effect of Moisture and FFA

Freedman et al, (1984), have noted that the starting materials used for transesterification of triglycerides should meet certain specifications. The glyceride should have an acid value less than 1, and all materials should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensated for higher acidity, but the resulting soaps caused an increase in viscosity or formation of gels and interfered with separation of glycerol and contribute to emulsion formation during the water wash [29, 32]. As little as 0.3% water in the reaction mixture reduces glycerol yields by consuming catalyst.

Other researchers have also stressed the importance of a nearly dry oil substantially free (<0.5%) of fatty acids [27, 29, 35].

In general up to 3% of FFA content, the reaction can still be catalyzed with an alkali catalyst without affecting the process negatively [43] but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerol or is washed out during the water wash.

CHAPTER 3

3. PILOT PRODUCTION PLANT AND METHODS

3.1 Introduction

In this Chapter, the materials and methods used for biodiesel production and quality assessment are described. The setups for biodiesel production and quality assessment are explained along with their operation. The Chapter proceeds in describing details of the procedures used to carry out the production processes in conjunction with the various experimental analyses present in the study. Prior to the biodiesel production process oil purification or neutralization was performed. Biodiesel production was performed using a thermostatically controlled water bath reactor. Sixteen experiments were carried out in order to optimize the production. The quality of the produced biodiesel is then assessed for different important parameters. In addition to see the effect of storage condition on the property of biodiesel, an experiment was carried out for different storage conditions.

3.2 Materials for Sample Preparartion

Reactants for sample preparation and biodiesel production

- Ethanol (C_2H_5OH): A 40 L of Ethanol alcohol with concentration of about 99.7% was supplied by ***Nile Petroleum PLC***. This ethanol alcohol of course was produced by ***Metahara* Sugar Factory** using its byproduct *molasses* as the main feedstock.
- Sodium hydroxide (NaOH), analytical grade, Concentrated Hydrochloric acid solution (HCL), Anhydrous Sodium Sulphate ($NaSO_4$): supplied by ***Gigra PLC*** a local chemical supplier**.**
- Jatropha Curcas Oil: A 20 L of purified JCO was supplied by Horn of Africa Environment Management and Research Center.

Reactants for physicochemical property tests

- Phenolphthalein: for PH indication
- Diethyl ether: for acid value determination

- KOH: for acid value determination

Apparatus for physicochemical property tests:

- digital scale
- Burrete, graduated in 0.1 ml
- Conical flask, of alkali resistance glass, 250 ml capacity
- Reflux condenser with interchangable ground-glass joints

Apparatus for *lab- scale* biodiesel production

- Stirrer motor with a capacity of 1000 rpm
- Water bath reactor with circulating thermostat and condenser
- Rotary distillation unit
- Electric oven

3.3 Small Scale Pilot Plant System Design

A complete system schematic is shown in Fig 3-1. The small scale pilot plant is designed for 200 L of biodiesel production per day. Here most of the equipments will be produced from sheet metal.

Biodiesel pilot plant

The pilot plant consists of crude oil tank, pure oil tank, reactors, ethoxide mixing tank, water tank, biodiesel washing tank, dryer tank, biodiesel storage tank, glycerine collector, and circulating pump. The plant is also equiped with ½” diametr pipe fittings valves and flexible hoses to assisst a controlable flow of reagents.

Oil Tanks

The crude oil is to be purified in a 275 lt cylindrical sheet metal tanker. This tanker is provided with the necessary hoses, inlet and outlet valves. At the bottom of crude oil purification tanker a 1000 lt cylindrical sheet metal container is attached for the purpose of collecting the slurry.

A 240 L pure oil storage tanker is connected with the purification tanker through the outlet valve of purification tank. Pure oil tanker, as the purification tank, is produced from a sheet metal.

Alcohol/ catalyst mixing tank

A 40 liter sheet metal mix tank of dry NaOH catalyst and ethanol is designed and produced. In this design it is assumed that the mixture is to be prepared on the ground manually by shaking. Therefore there will be no need of a stirring mechanism.

Main reactor

The main types of reactors in small scale industry are batch reactors. This approach is more flexible as it allows the process parameters to be adjusted for each batch so it is relatively easy to compensate for differences in feedstock characteristics [33]. Based on this thought the research utilizes tanks and drums that served as batch reactors. The reactor´s outside cover is shielded by an insulator in order to keep up inside reaction temperature at the required temperature. A conical bottom is allowed for easier separation and draining of the denser glycerin product. Inlet and outlet valves are provided for oil & ethoxide admission and glycerin & biodiesel exit respectively. On the top of the rector motor connected with a propeller welded at one end of a stainless steel rode is installed so as to assist the mixing of oil and ethoxide through agitation.

Water wash tank

The removal of any remaining trace contaminants takes place in the 275 lt heated and insulated wash drum. This step is critical for meeting fuel quality specifications. A hot water tanker with 48 lt volume is installed to deliver hot and clean water for washing. A mist apparatus will be built from ½-inch pipe with fogger mist nozzles deliver pure water to the top of the esters, The unit was shaped in a cross pattern to lay flat across the top of the tank. Following mist application, a solvent resistant air stone was used for continuous overnight air bubbling, which leaves the fuel polished and almost clear.

Drying tank

A final drum tank was designed for drying the esters. The ester is planned to be heated through a pipe-plug immersion heater while re-circulated within the drying drum. The heated esters will be sprayed tangentially to the upper inner surface of the open drums. This spraying of the hot esters allowed maximum surface area for water evaporation. The drying process required approximately one hour from the time the oil is heated to about 70 ºC depending on humidity and ambient temperature.

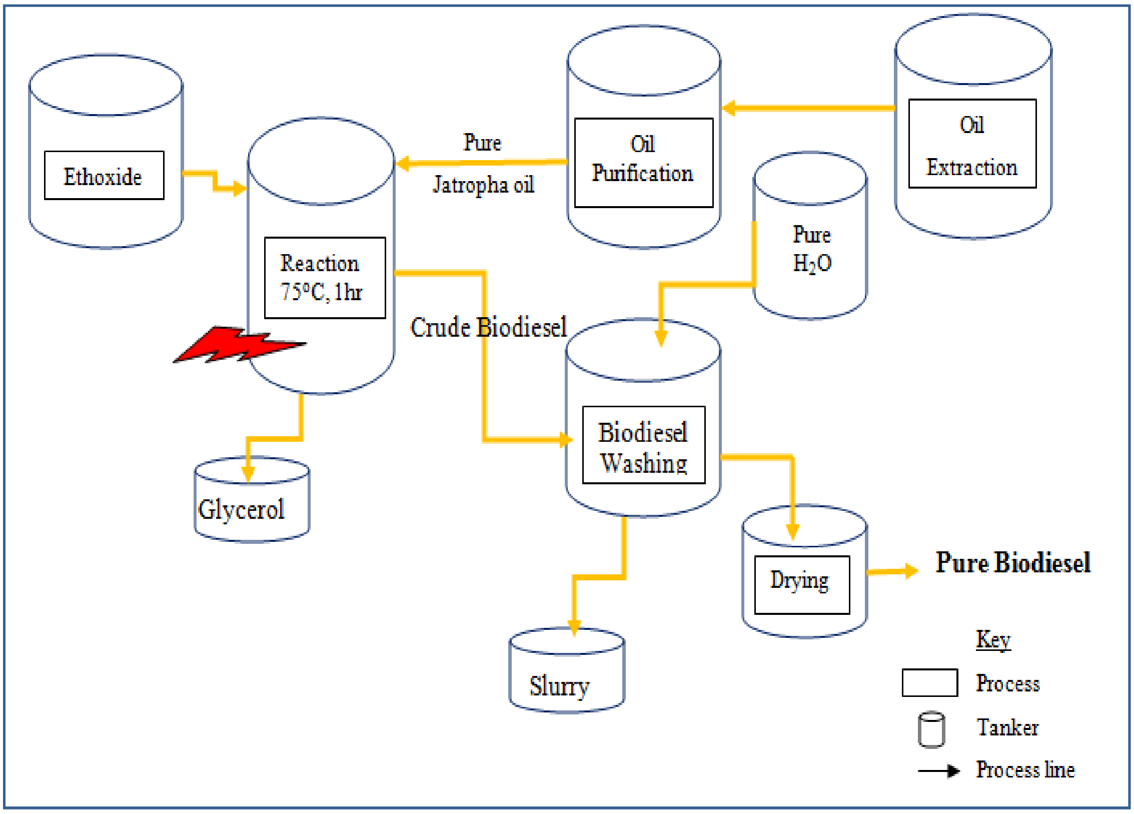

Fig 3-1 Biodiesel Production Process Flow Chart

Fuel storage

The finished biodiesel will be filtered using a nylon filter and stored in a 660 L corrosion resistant painted sheet metal tank until delivery is made.

Note: even though the pilot plant is developed this way to produce 200 liters of biodiesel per day, the production is not tested yet through this plant. This is mainly because:

a. A lab scale production has to be performed prior to pilot scale production in order to investigate the theoretically claimed results practically and

b. The result of this lab scale production has to be standardized so that it will be used in controlling the quality of the pilot plant output.

More over there is also a budget and time constraint to test the production in the designed pilot plant.

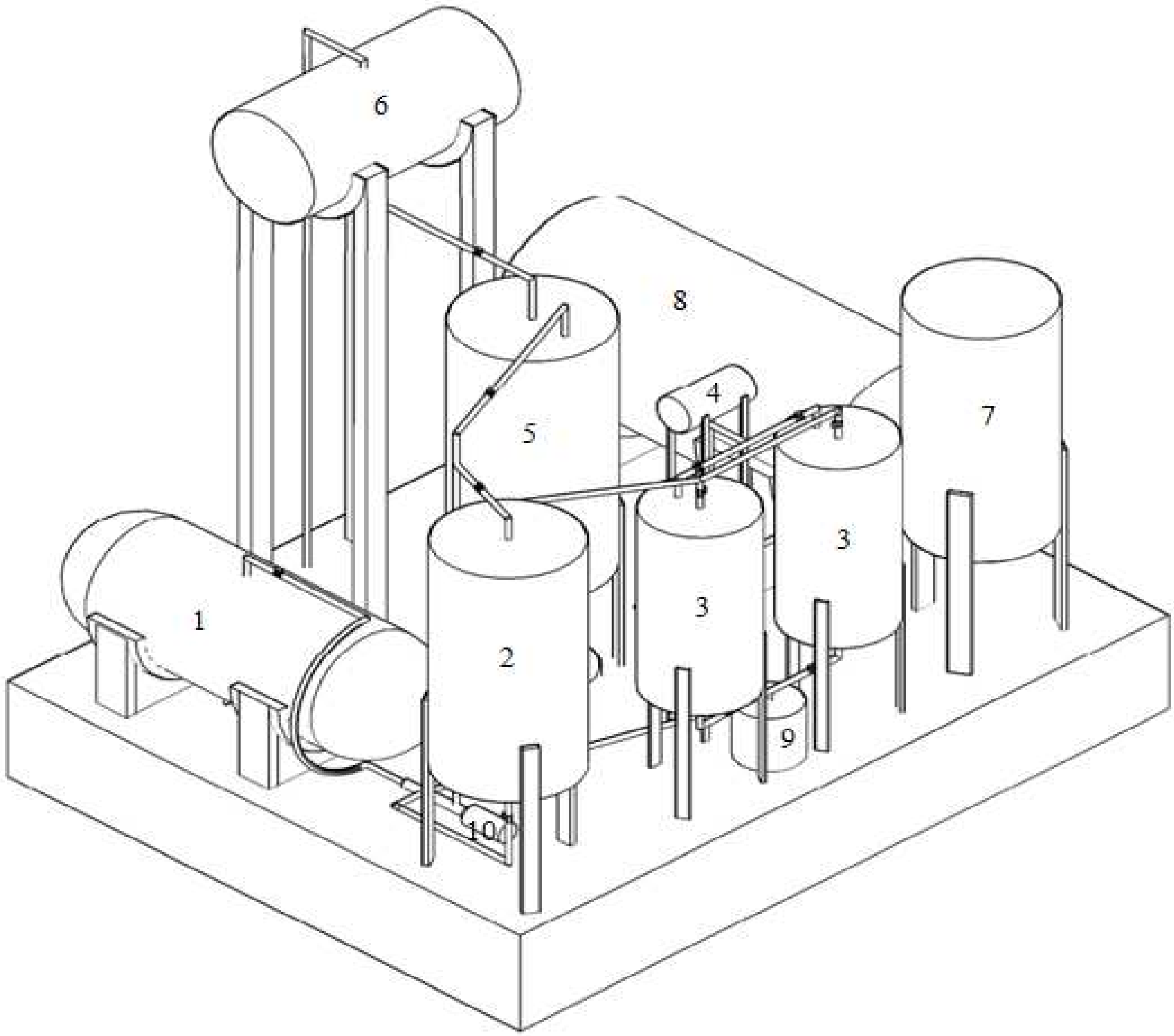

Fig 3-2 Biodiesel Pilot Plant

1. Crude Oil Tank
2. Pure Oil Tank
3. Reactors
4. Ethoxide Mixing Tank
5. Biodiesel Washing Tank
6. Water Tank
7. Dryer Tank
8. Biodiesel Storage Tank
9. Glycerine Collector
10. Circulating Pump

3.4 Methods

3.4.1 Characterization of physicochemical properties of JCO

Certain physicochemical properties of the supplied oil has to be determined prior to the production process. The feedstock status determination helps not only to know the condition of the oil but also helps to make certain decision on whether it requires further treatment or not. The main physicochemical properties that have to be determined are percentage of FFA content, acid value, relative density, kinematic viscosity, specific gravity, and saponification number. These parameters directly or indirectly affect the quality of the final product/biodiesel.

Sample Preparation

According to the nature of the determination to be carried out, the sample made homogeneous by separating the substances insoluble in the particular Jatropha oil or by eliminating water. The sample preparation starts from rendering it as homogeneous as possible by turning the container upside down for several times. For those determinations in which the result might be affected by the possible presence of moisture in the oil to be analyzed (Acid value), the sample should be previously dried. For this purpose the sample which was thoroughly mixed is placed in an electric oven at 50 ºC after adding anhydrous sodium sulphate (Na_2SO_4) in the proportion of 1 g per 10 g of JCO[a]. The sample heated with sodium sulphate is vigorously stirred and filtered with vacum filter.

1. Determination of specific gravity

A Specific gravity (SG) or relative density (RD) of an oil at a given temperature is the ratio of the mass in air of a given volume of the oil at that temperature to that of the same volume of water at 20ºC [33]. Usually it is expressed as “sp gr @ t°C/20°C”. Hydrometer was used to measure the SG of the oil at 20 ^{0}C. The sample was filled into graduated cylinder (100 ml) and its temperature was recorded.

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[a] This ratio is based on Ethiopian Standards for edible oil and fats (ES B.K8.002)

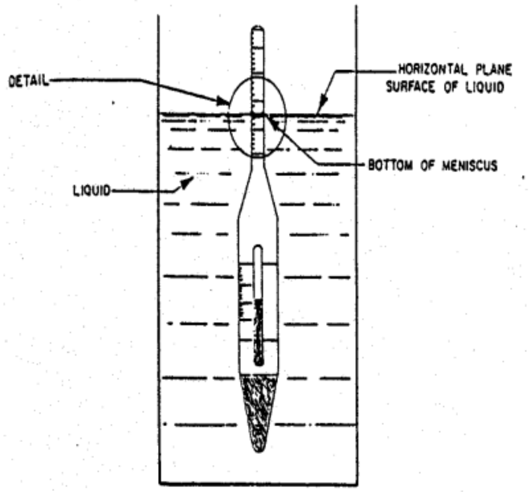

Fig 3-3 Hydrometer for measuring specific gravity[a]

2. Removal of free fatty acids with caustic treatment

While using feedstocks with a considerably higher content of FFA (in which % FFA greater than 1), employing a neutralization process using a base catalyst to deliberately form soap from the FFAs and removing the soap is the easiest and the cheapest alternative [17, 43].

Fig 3-4 shows the schematic diagram of neutralization process. In the process the soap is recovered, the oil dried, and then used in a conventional base catalyzed system.

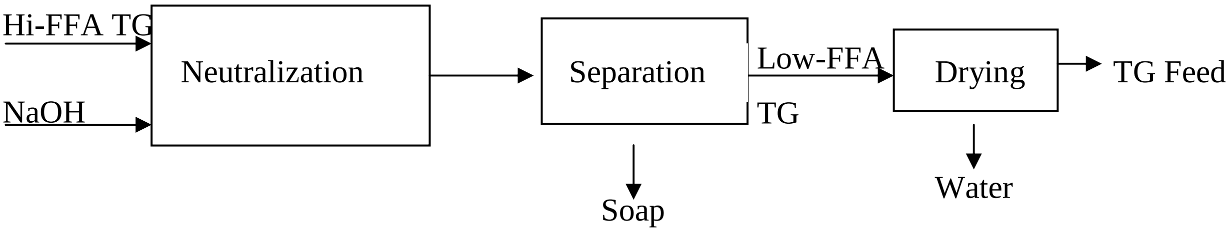

Fig 3-4 Removal of free fatty acids with caustic[b]

In this neutralization treatment a 0.5 N (Normality) NaOH solution was added to the crude oil (which was heated to approximately 70 ^{o}C). A constant stirring at 800 rpm is applied for thorough mixing of the two phases. Sodium chloride (about 10% of the weight of the oil) was added to help settle the soap formed. After an hour of mixing

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[a] Adopted from J. Van Gerpen, et al. ‘Biodiesel Analytical Methods’, 2004
[b] Adopted from J. Van Gerpen et al., ‘Biodiesel Analytical Methods ’, 2004

the mixture was transferred into a separating funnel and allowed to stand for 1 h. The soap formed was separated from the oil. Washing is then followed by adding hot water gently again and again until the soap remaining in solution was removed. The neutralized oil was then drawn off into beaker. The appropriate amount of alkaline solution (NaOH) required to neutralize the free fatty acid was calculated as follows:

$$L = \frac{\rho_{of\ oil} * 1000}{MN} \qquad \text{eq 1}$$

Where:

L = appropriate amount of N molar aqueous NaOH solution [L]
ρ = Density oil [gm / lt]
M = molecular weight of fatty acid (taking oleic acid’s molecular weight=278)
N = concentration of aqueous NaOH solution.

3. *Acid Value Determination*

Acid value (or "*neutralization number*" or "*acid number*" or "*acidity*") is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point [43]. It is used to quantify the amount of acid present, for example in a sample of biodiesel. In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. Applying this principle acid value for JCO was determined using the AOCS standard method (Ca-5a-40) [52]. According to this method, about 2 g of a purified JCO was thoroughly mixed with a mixture of 25 ml of neutralized[a] ethanol alcohol and 25 ml diethylether followed by two drops of phenolphthalein indicator in a titration flask and then titrated against 0.01 N aqueous solution of KOH until pinkish color appeared. From the titrated data acid value was calculated using the following equation:

$$AV = \frac{N \times V \times M}{W} \qquad eq\ 2$$

Where

N The normality of aqueous solution of KOH

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[a] Neutralization is required since alcohols get acidic for prolonged storage.

V Volume of titrant used for titration [ml]

M Molecular weight of KOH

W The weight of oil sample

4. *Free Fatty Acid (FFA)*

Percentage free fatty acid/FFA content of the oil was calculated empirically using the acid value previously determined as follows:

$$\% FFA = \frac{AV}{0.503} \qquad \text{eq 3}$$

Where:

% FFA = Percentage free fatty acid content in terms of oleic acid [33].

AV = Acid value of the oil.

5. *Kinematic Viscosity*

A digitalized Vibro-viscometer was employed to determine the viscosity of oil. The sample was kept in the bath for 30 minutes to reach the required temperature. The reading was recorded for a fixed volume of liquid. Since the reading of the Vibro-viscometer was dynamic viscosity the value had to be corrected to find the kinematic viscosity using the following equation [42]:

$$\nu = \frac{\eta}{\rho} \qquad eq\ 4$$

Where:

η dynamic viscosity of the oil

ρ density of the oil

ν kinematic viscosity

Fig 3-5 Vibro-Viscometer

3.4.2 Laboratory Scale Biodiesel Production

The biodiesel produced in this work was prepared using a purified JCO, a locally produced ethanol alcohol (approximately 99.7%) and analytical grade sodium hydroxide. Diferent reaction parameters, such as alcohol to oil molar ratio and reaction temperature, are considered while producing the biodiesel. The parameters considered will be discussed in the following section.

a) Experimental Design

An optimization for percentage yield of biodiesel was designed for two selected factors: ethanol to JCO molar ratio and reaction temperature. The selection of parameters levels was based on previous research works and practical considerations. The upper temperature level (78°C) was the theoretical boiling point of ethanol, and catalyst concentration of 1.5 % by weight of oil was based on literature data [18]. The lower molar ratio (6:1) was the theoretically declared maximum yield giving molar ratio [43], and the upper molar ratio (9:1) was based on previous research. The reaction time and mixing intensity were fixed at 3 hours and 600 rpm respectively for all experimental runs. The order for conducting the 16 experimental runs was presented in Table 3.1 using the selected levels for reaction temperature, molar ratio of ethanol to JCO, NaOH concentration, reaction time, mixing intensity, and used sample quantity.

Table 3-1 Order for conducting experimental runs

No	**Temp [°C]**	**MR**	**Catalyst Conc.**	**Used oil per test [ml]**	**Used Ethanol per test [ml]**
1	55	6:1	1.50%	300.0	108.6
2	65		1.50%	300.0	108.6
3	70		1.50%	400.0	144.8
4	78		1.50%	300.0	108.6
5	55	7:1	1.50%	300.0	126.7
6	65		1.50%	300.0	126.7
7	70		1.50%	300.0	126.7
8	78		1.50%	300.0	126.7
9	55	8:1	1.50%	400.0	193.0
10	65		1.50%	400.0	193.0
11	70		1.50%	400.0	193.0
12	78		1.50%	337.0	162.6
13	55	9:1	1.50%	400.0	217.1
14	65		1.50%	400.0	217.1
15	70		1.50%	400.0	217.1
16	78		1.50%	400.0	217.1

b) *Experimental set-up*

The transesterification reaction system utilized in this work is shown in Fig 3-6. The experimental set up consists of a 1000 ml two necked water batch reactor which is equipped with a motor (IKA WERKE, max 2000 rpm) fitted with stainless steel rod stirrer provided the mixing requirement and condensing coil. The reactor (borosilicate glass) was immersed into a constant temperature water bath equipped with a thermostatically controlled heater. Sixteen reactions were carried out over the entire duration of experimental work.

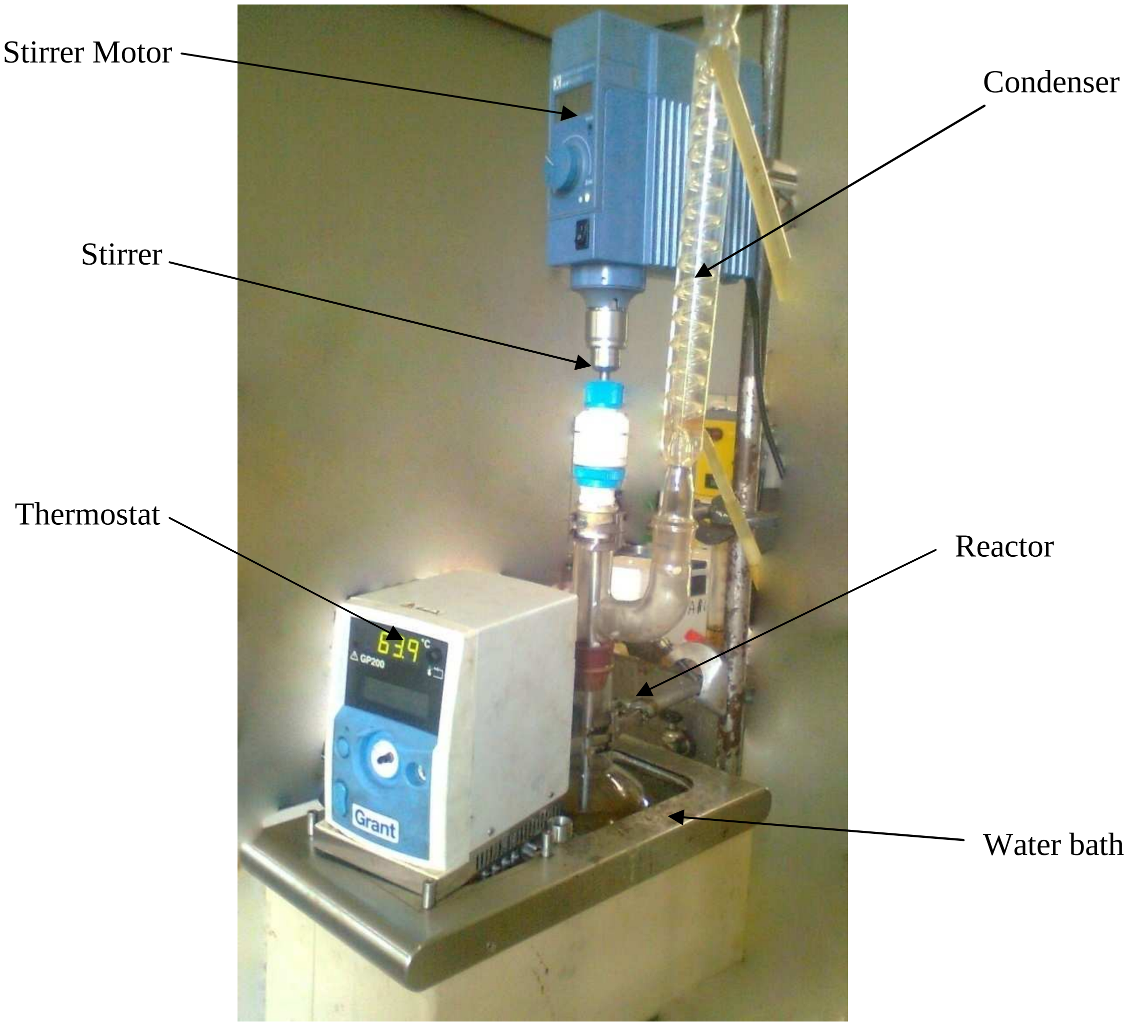


Fig 3-6 Experimental set-up used

c) Production Procedure

Ethanol and sodium hydroxide mixture was prepared as per the requirement. This mixture was agitated continuously until all the sodium hydroxide dissolved completely. The reactor was then charged with required amount of JCO and the ethoxide solution as per the design. Then the reactor assembly was heated to the desired temperature by using the circulating thermostat. Mixing, assisted with mechanical stirrer motor, was started immediately by gradually increasing the intensity to 600 rpm. After three hours of the reaction time the resulting mixture was neutralized by adding about 1 g of tannic acid. Then the mixture was transferred to a rotary evaporator unit so as to recover for the excess alcohol. The mixture, whose alcohol was recovered, was then transferred to a clean separating funnel and allowed to separate.

After the separation is completed the biodiesel layer was collected and transferred to another separation funnel for washing. The biodiesel layer was purified by washing with warm water [43] to remove ethanol, residual catalyst and soaps. A water wash solution at the rate of 28% by volume of oil and 1 g of tannic acid per liter of water is added to the ester [24]. During the washing process, gentle agitation was applied to avoid the emulsion. After separation of the layer for 30 minutes, the wash water layer was drained off from the bottom of the separating funnel. The washing process was repeated until the ester layer became clear. About five drops of phenolphthalein solution was added while washing is carried on as a PH indicator. The washing was continued until most of the unreacted oil, catalyst, alcohol, and trace glycerine are washed away. After washing process, the biodiesel was dried using anhydrous sodium sulphate to take away trace of water in the biodiesel. The sodium sulphate was then filtered using vacuum filter. For further drying the biodiesel was allowed to stay in an oven for several hours at 50 ^{0}C [74].

Fig 3-7 Vacuum filter

3.4.3 Post-Production Quality Determination

Post production quality determination is nothing but the physicochemical properties characterization of the produced biodiesel. The characterization involves determination of specific gravity, acid value, kinematic viscosity, and flash point of the biodiesel.

A. *Specific gravity (at 15°C), kg/m^3*

The procedure described in section 3.4.1 was used to determine the specific gravity of biodiesel.

B. *Kinematic viscosit, mm^2/s*

The procedure described in section 3.4.1 was used to determine the kinematic viscosity of biodiesel.

C. *Flash point (°C)*

The flash point of the biodiesel was determined using open cup method. The cup was filled with the biodiesel (about 75 ml) and the cup was heated by a Bunsen burner. A small open flame was maintained from an external supply of LPG. Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached the surface of the oil catch the flame. Therefore the temperature at which the surface of the oil catches the flame was noted and reported as flash point temperature.

D. *Acid value (mg KOH/g)*

The procedure described in section 3.4.1 was used to determine the acid value of biodiesel.

CHAPTER 4

4. RESULT AND DISCUSSION

This chapter discusses the results obtained from the experimental runs performed on the crude/purified JCO. The experiments were performed in three steps.

- Step 1 (Crude oil status determination)-An experimental run was conducted to perform a pre-production quality assessment on the crude JCO. Under this experimental run the acid value, kinematic viscosity, specific gravity, and the free fatty acid content of the crude oil were determined.
- Step 2 (Crude oil Purification)-In this step the crude oil was purified/neutralized using caustic treatment method. Following the caustic treatment an experimental run was performed so as to determine the acid value, the kinematic viscosity, specific gravity, and the free fatty acid content of the purified oil.
- Step 3 (Biodiesel production and characterization)- Several experimental runs were conducted under this step so as to determine the best yield giving parameter combinations and also to assess the post production quality of the produced biodiesel.

4.1 Physicochemical Properties Analysis of Crude and Purified JCO

The acid value, percentage FFA content, kinematic viscosity, and specific gravity of the crude as well the purified jatropha oil are the major physicochemical properties those were investigated as the first step of the experimental work and results of the investigation are presented in Table 4-1.

Specific gravity of the crude Jatropha oil was in agreement with the result reported by [25] and [45] which was 0.903 and 0.92 respectively. Whereas the kinematic viscosity of the crude Jatropha oil was a little lower than the value reported by [62] but still in agreement with results obtained by [25, 45, 74] which was around 41.5-43 mm^2/s at room temperature. As the result indicates the caustic treatment had no effect on specific gravity and kinematic viscosity.

Table 4-1 Physicochemical properties of jatropha oil

Properties	Crude Oil	Purified Oil	Unit
Color	Golden yellow	Light yellow	
Specific Gravity	0.91	0.90	---
Kinematic Viscosity @ 20 ^{0}C	44.25	42.34	mm^2/s
Acid Value	5.01	1.35	mg KOH/g
FFA %	2.52	0.68	---
Physical state at room temperature	Liquid	Liquid	

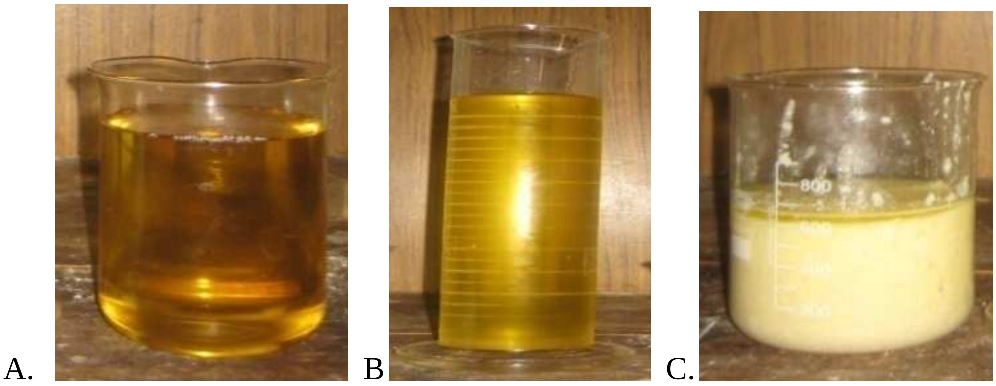


Fig 4-1 Components of oil purification process (A) Crude oil (B) Purified oil (C) Soap

The acid value of the crude Jatropha oil was a little higher than the value reported by [1] and [49] which was (4.24-2.59 mg KOH/g). This is because the oil used in this research was stored for a long time (more than six months) and due to this prolonged storage as well the intrusion of contaminants the oil got deteriorate [61].

According to Table 4-1 the acid value of the CJCO was not in the range, which was acceptable for base catalyzed transesterification reaction (acid value of oil should be below 2mg KOH/g) and preferably < 0.05 %, according to ASTM and EN standards [42]. Therefore the oil was treated to reduce the acid value to 1.35 mg KOH/gm which was less than the required acid value to use for base catalyzed transesterification process.

In general the reason for the difference in physicochemical properties of CJCO of this work and others mainly relied on the chemical composition of the crude oil which is definitely influenced by:

1. The plant species
2. Agro-climatic conditions
3. Oil processing mechanism employed (e.g. mechanical extraction/solvent extraction)
4. Oil handling (e.g. short/prolonged storage, stored in closed/open container)

4.2 Biodiesel Yield

The biodiesel yield was investigated mainly for the two major parameters namely ethanol to oil molar ratio and reaction temperature. In this investigation the reaction time, catalyst concentration, and mixing intensity kept constant (3 hours, 1.5% by weight of oil, and 600 rpm respectively) for all experimental runs. The biodiesel was synthesized using batch wise transesterification process.

After the transesterification reactions were completed, the resulting biodiesels were not separated from the glycerol easily. It was the major hurdle that was faced while doing this experiment. The main reason for this was the far better solubility of ethanol in the ethyl ester phase when compared to methanol. Another important reason is the higher degree of saponification during ethanolysis. For these reasons phase separation of glycerol required a little modification than the classical biodiesel production process. Before the transesterified mixture was subjected in to rotary evaporation unit for ethanol recovery the mixture was neutralized by adding about 0.8 g of tannic acid, an inorganic acid, to hinder the effect of the catalyst [18]. Easy agitation was applied to speed up the solubility.

After the neutralization was completed the mixture was subjected to the rotary evaporator (working with water bathed heater) to recover the excess alcohol. Through this process about 30 % of the excess alcohol was able to recover. After the alcohol recovery was done the mixture was then centrifuged at 4000 rpm for 20 minutes. After centrifugation the glycerol were settled at the bottom of the centrifuging tube, the biodiesel were separated from the glycerol and washed several times with warm water (ca 50 ^{0}C) until the biodiesel got clear. The biodiesel then dried by adding anhydrous sodium sulphate (10 % by weight of biodiesel) and the final product, dried biodiesel, were measured. The biodiesel yield (percentage by volume of the oil used) for the experiments is presented in Table 4-2. Experiments 15, 1, and 3, render the highest biodiesel yields.

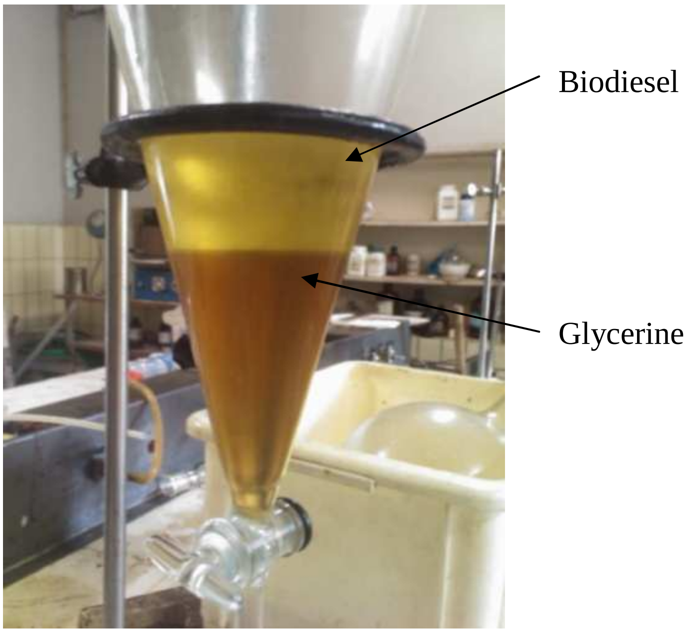
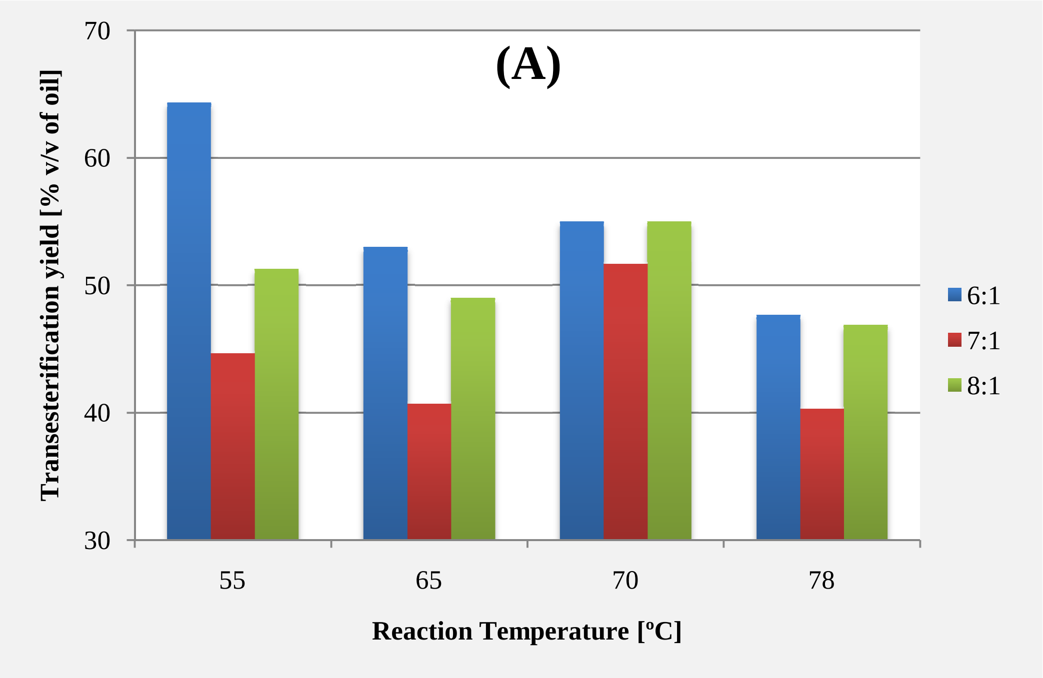


Fig 4-2 Transesterification phase separation

4.2.1 Effect of temperature

The experimental results show that the biodiesel yield was affected by reaction temperature.

Fig 4-3 clearly shows the effect of reaction temperature for the 4 ethanol to oil molar ratios. At a lower reaction temperature the yield is higher for a lower ethanol to oil molar ratio. As the reaction temperature increased by 10 ^{0}C the yield decreased irrespective of the change in molar ratio (refer Fig 4-3). At a reaction temperature of 70 ^{0}C the yield increased for almost all molar ratios. This is due to the fact that at the altitude where the experiment was carried out (Addis Ababa) the actual boiling point of ethanol is around 72 ^{0}C. Therefore near to this temperature the transesterification process got completed with less saponification. But at a maximum reaction temperature (a theoretical boiling temperature of ethanol, 78 ^{0}C) the transesterification process yield was too low. This is because at this temperature the saponification is higher and this hinders the separation of glycerol. The phenomenon expressed above is true for the tested molar ratios.



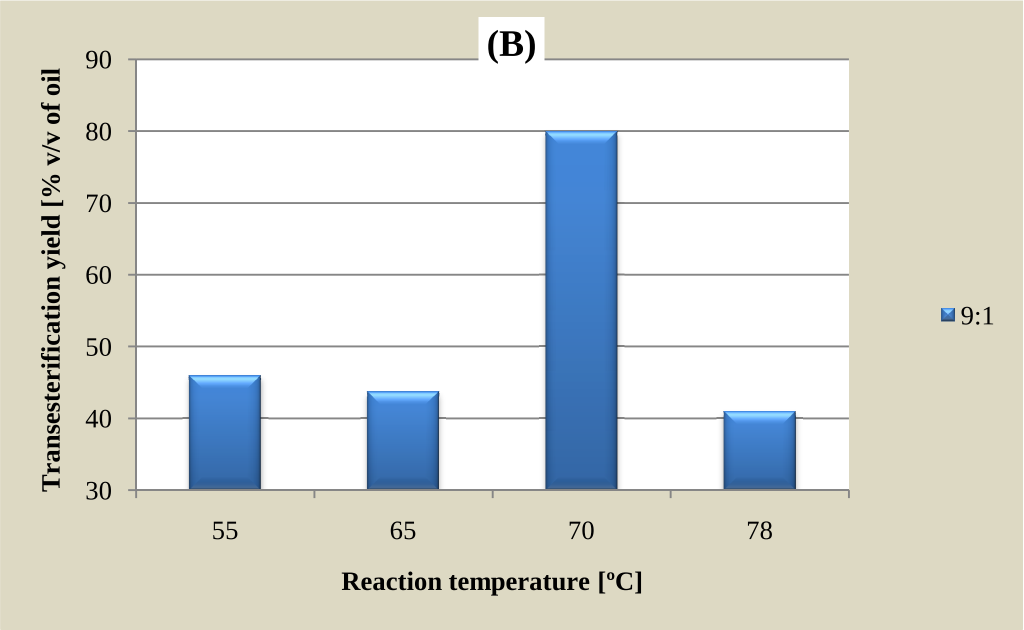


Fig 4-3 Effect of reaction temperature on transesterification yield. (A)-for molar ratio 6:1, 7:1, and 8:1 (B)-for molar ratio 9:1

Table 4-2 Results of the experiments

Expe. No	**Temp [°C]**	**MR**	**% Yield**	**[a]Specific gravity**	**[b]Viscosity [mm^2/s]**
1	55	6:1	64.33	0.86	4.01
2	65		53.00	0.86	4.09
3	70		55.00	0.86	4.40
4	78		47.67	0.86	4.07
5	55	7:1	44.67	0.86	4.13
6	65		40.67	0.86	4.09
7	70		51.67	0.86	4.38
8	78		40.30	0.86	4.17
9	55	8:1	51.25	0.86	4.43
10	65		49.00	0.86	4.21
11	70		55.00	0.86	4.28
12	78		46.88	0.86	4.45
13	55	9:1	46.00	0.86	4.26
14	65		43.75	0.86	4.15
15	70		80.00	0.86	4.13
16	78		41.00	0.86	4.43

4.2.2 Effect of molar ratio

To optimize the amount of ethanol required for the reaction, experiments were conducted with 6:1, 7:1, 8:1, and 9:1 molar ratio of ethanol to oil. The results of this study are presented in Fig 4-4. At a reaction temperature of 55, 65, and 78 ^{0}C the effect of molar ratio is somehow negative. For such temperatures a better yield was observed for the lowest molar ratio. This was because the saponification effect is lower at a lower molar ratio. Hence as the concentration of the alcohol increases to 7:1 the yield decreases. Similar effect was also observed for change in concentration of alcohol from 8:1 to 9:1.When it comes to a temperature of 70 ^{0}C the effect of molar ratio is positive.

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[a] Specific gravity at room temperature (20 °C)

[b] Kinematic viscosity at 40 °C

Especially for molar ratio 7:1 and beyond as the ethanol concentration increases the transesterification yield also increases. This is for the reason that the increase in ethanol concentration reduce somehow the emulsification of the biodiesel with the glycerol, and make the separation a little bit easier.

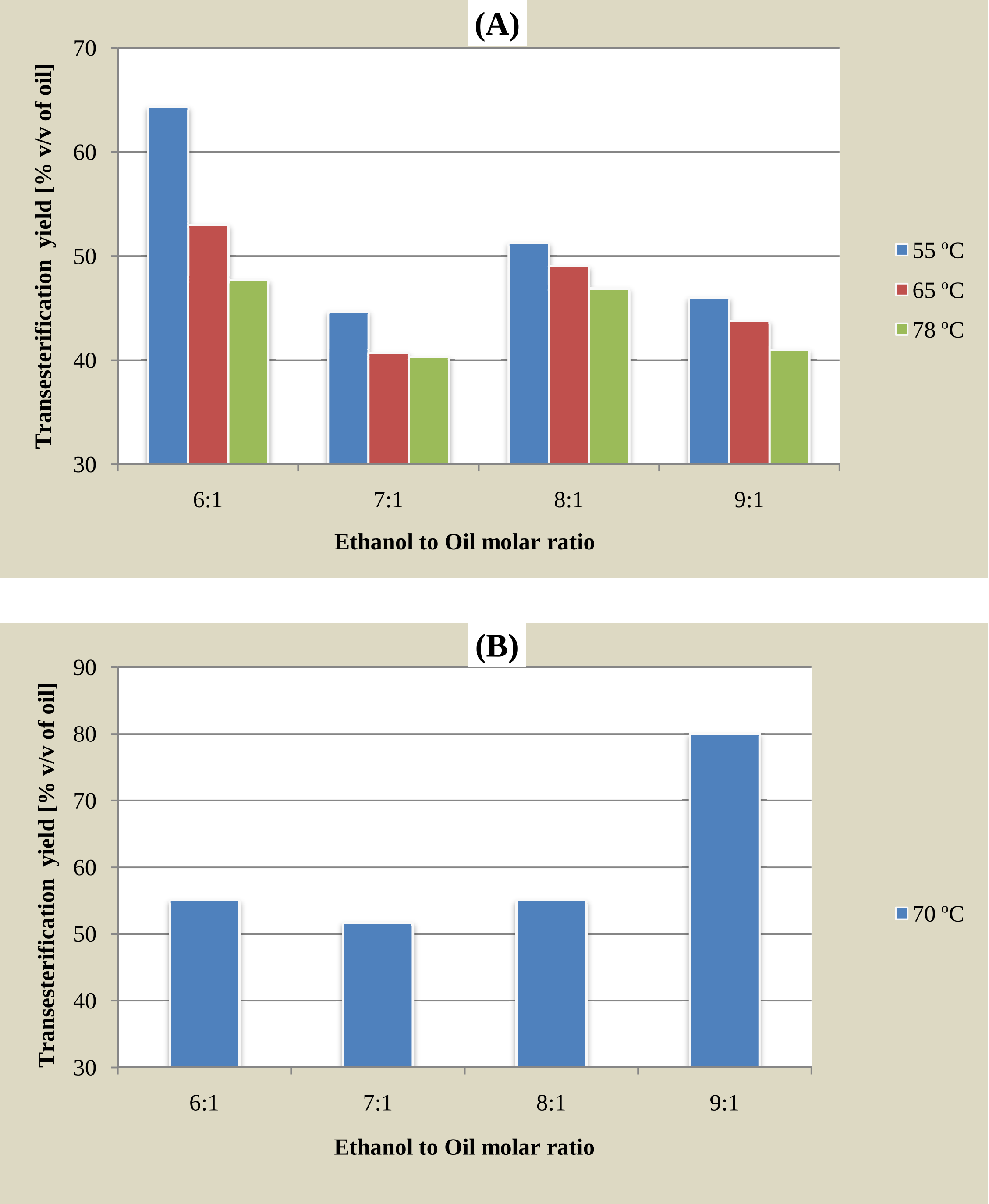

Fig 4-4 Effect of ethanol to oil molar ratio on transesterification yield. (A)-for 55, 65, and 78 °C. (B)- for 70 °C

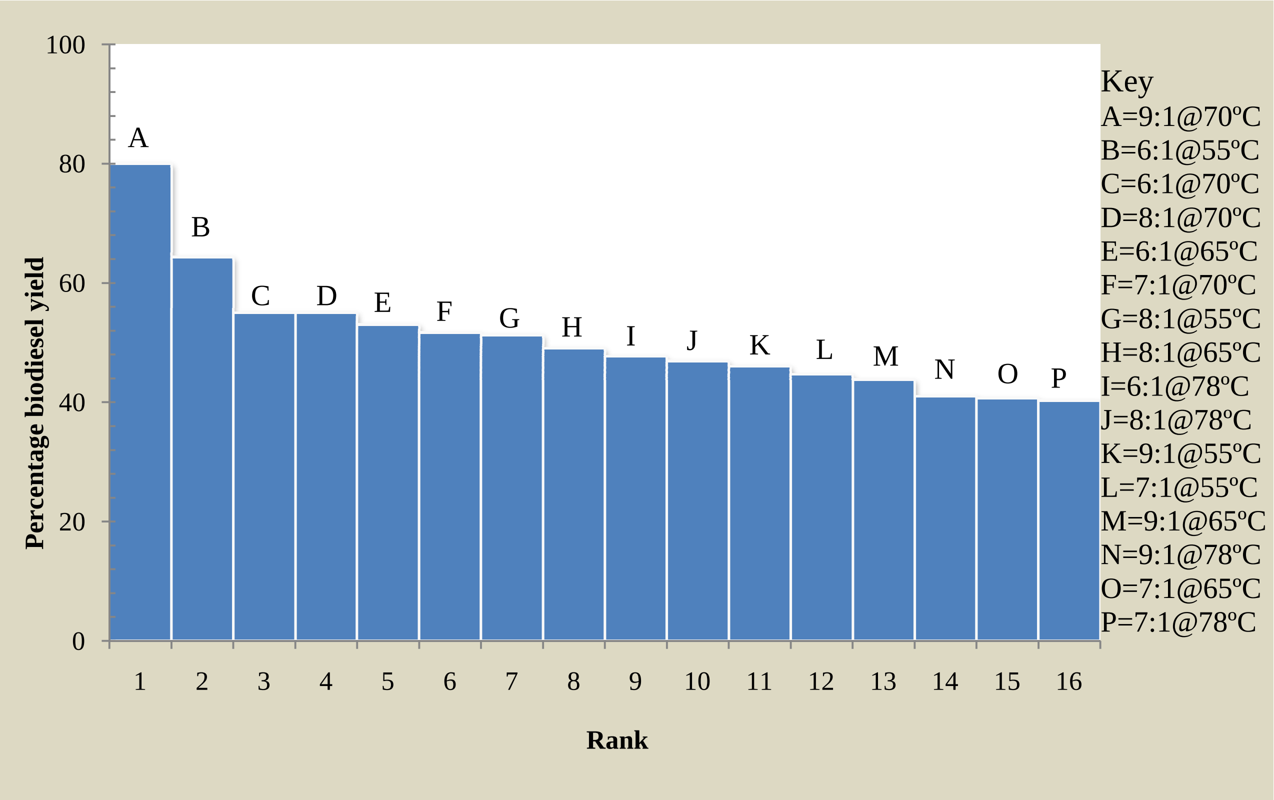

Fig 4-5 Summary of the experimental results

Fig 4-5 summarizes the transesterification yield of the 16 experimental runs. The results are arranged in descending order making the yield obtained at a molar ratio of 9:1 and reaction temperature 70 ^{0}C the top by 80 % yield and the yield obtained at a molar ratio of 7:1 and reaction temperature 78 ^{0}C the bottom by 40.3 % yield (for details of the yield of each experimental runs please refer Table A-5). From Fig 4-5 it is possible to see that the average yield for the 16 experimental runs is around 51 % with a standard deviation of 10.1. This clearly indicates that most of the experiments are giving a yield more than 40 % lower than the claimed results of [57] and [60]. There could be so many reasons for this but the main possible reasons are:

A. ***The difference in alcohol used***: most foreign research works on biodiesel production employed methanol instead of ethanol for its abundance in their local market. Fortunately methanol has almost no problems related with saponification and separation because of this reason a better yield could be found with less sophisticated production process.

B. ***Inaccuracy of production equipments***: most of the laboratory equipments used were not that much accurate for experiments that requires too much care. The water bath was open and because of this there was a possibility of water vapor intrusion in to the reactor through the opening of the condenser tube (refer Fig 3-6).

C. ***Hygroscopic characteristics of ethanol***: in ethanolysis process the ethanol alcohol must be as dry as possible, some researchers even fix the water content to less than 0.5 % [18, 29]. Ethanol by nature is too hygroscopic it could even absorb moisture from the surrounding humid air; due to this property of ethanol more water was present in the reaction than the minimum required value. The presence of water cause hydrolysis of triglycerides, this intern reduces the ester yield. In the laboratory where the experiments done, it was so hard to keep the alcohol perfectly anhydrous.

D. ***Inappropriate equipment***: one of the equipment used in the biodiesel production was a rotary evaporator, for ethanol recovery. So as to distillate the excess ethanol from the transesterified mixture the rotary evaporator had to supply a temperature at least equivalent to the actual boiling temperature (which in this case was about 72 ^{0}C) and the mixture had to stay in the evaporator until enough of the excess ethanol was recovered. This of course has taken a longer time good enough to distort the reaction temperature and speed up the saponification reaction. Since there was still unrecovered ethanol, unreacted oil, and most importantly a catalyst to undergo a saponification reaction at that temperature. *This phenomenon actually was the major reason for the reduction of the yield.*

4.3 Physicochemical Properties of Biodiesel

The top three tests, based on their yield, were selected and the production was repeated with the same parameters. The yields were determined and no significant change was observed. The quality of biodiesel is very crucial for the performance and emission characteristics of a diesel engine. Thus these three jatropha curcas biodiesel produced were engaged for pro-production quality testing to examine the physicochemical properties of the biodiesel samples. The characterization was performed for the four properties namely density, kinematic viscosity, acid value, and flash point. These properties were selected for two main reasons. One because they are the defining properties of biodiesel and the other is because of the limitation of resource to perform other tests. The results were then compared with ASTM D6751-02 and EN 14214 standards. Table 4-3 depicts the result of pro-production quality assessment.

The density of the biodiesel produced for experiment 15, 1, and 3 were 0.86, 0.86 and 0.86 g/ml, which was slightly lower than the value reported by [60] and [62] which was 0.88. However these results are still within the ASTM standard value which is between 0.86 and 0.90 g/ml.

Table 4-3 Physicochemical properties of the produced biodiesels

Properties	**JOEE**			**ASTM D6751-02**	**EN 14214**	**Units**
	Exp 15	Exp 1	Exp 3			
Density @ 15 ^{0}C	0.86	0.86	0.86	--------	0.86 – 0.90	gm/ml
Kinematic Viscosity @ 40 ^{0}C	4.13	4.01	4.40	1.5- 6.0	3.5 – 5.0	mm^2/s
Acid Value	0.71	0.63	0.77	0.8 max	0.5 max	mg KOH/g
Flash point	173.3	187.7	183.7	130 min	101 min	^{0}C

The density shows about 5.5 % reduction from the original oil for experiment no 15, 1, and 3 after the transesterification process.

The kinematic viscosity measured for the biodiesel measured for experiment 15, 1 and 3 were found to be 4.13, 4.01 and 4.4 mm^2/s respectively. The kinematic viscosity of the original oil at 20 ^{0}C was more than 40 mm^2/s. As the result indicates the ethanolysis significantly reduces the kinematic viscosity of the primary jatropha oil by approximately one-tenth of its initial value. The results are still within the limit of the ASTM specification i.e. (1.9 – 6.0 mm^2/s).

The flash points of the biodiesels were determiner according to the standard procedure for flash point measurement of flash point of biodiesel, i.e. ASTM D93. The observed flash point of the biodiesels fort test 15, 1 and 3 (refer Table 4-3) were 173, 187.7 and 183.7 ^{0}C, respectively. The resulted flash points for the biodiesels were within the specified standards limit of ASTM i.e. (min 130 ^{0}C). As the result shows the flash points of the three tests were 51^{0}C above the minimum requirement. It is the indication of the purity of the biodiesel from excess ethanol residue.

The acid value for the experiments 15, 1 and 3 were found to be 0.71, 0.63 and 0.77 mg KOH/gm respectively. It is clear to see from the result that the ethanolysis process successfully reduces the acid value of the initial oil. Even though the result shows that the acid values for the three tests are within the ASTM limit they are slightly higher than the value reported by [62] which was 0.4. This is of course due to the difference in feedstock property, the material used in the production, and the production process.

CHAPTER 5

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this research biodiesel was prepared at different reaction parameters from Jatropha oil and ethanol alcohol with sodium hydroxide catalyst in a laboratory scale. Reaction temperature and ethanol to oil molar ratio were the considered parameters for the optimization investigation. Under this investigation two parameters with four levels were considered. From the experimentation it was found that maximum biodiesel yield of 80 % was obtained by using reaction parameters such as ethanol to oil molar ratio of 9:1, NaOH 1.5 %, reaction temperature of 70 ^{0}C and reaction time of 180 minutes followed by a yield of 64.33 % at 6:1 molar ratio & 55 ^{0}C and 55 % at 6:1 molar ratio & 70 ^{0}C.

After the production is completed the physicochemical properties of biodiesel prepared were tested to check whether the products could satisfy the international standard or not. For this test only the top three products were selected right only for the sake of minimizing cost and time. The tested physicochemical properties for the selected were found to be within the ASTM specified limit.

From the lab scale production of biodiesel, the ethanolysis process was found to be a bit difficult, for the reason explained in section 4, than the ordinary methanolysis process. Because of that reason the yield of ethanolysis processes of biodiesel production were lower than the value reported by other researchers. To increase the separation efficiency, it was necessary to modify the classical biodiesel separation method by adding two intermediate processes namely neutralization and ethanol recovery; though perfect separations were not achieved yet.

Generally speaking, from this research one can say that ‘YES IT IS POSSIBLE TO PRODUCE A BIODIESEL FROM JATROPHA OIL AND FROM LOCALLY AVAILABLE, CAUSTIC SODA AND ETHANOL ALCOHOL THAT CAN MEET INTERNATIONAL STANDARDS!!’

5.2 Recommendations

Since Ethiopia has the potential of harvesting about 46.6 million tons of jatropha seed per year plus ethanol is being produced locally as by product sugar production, it is highly recommended to use these resources in producing a biodiesel, an eco-friendly fuel, that can substitute a fossil based petro diesel. This research confirmed the possibility of producing biodiesel from those local resources.

Even though the result of this study was satisfactory, on the basis of producing biodiesel from those local resources and meeting an international standard, the yield of every experimental runs was not as good as the expected. Therefore the following points are recommended in order to step up the yield of the ethanolysis process:

1. The experimental set up should be absolutely free of water; this could be achieved by using an oil bathed reactor which is perfectly sealed from introduction of any contaminants. If water by any means introduced into the reactor the yield will decreases due to soap formation.
2. The ethanol alcohol which supposed to be used in the transesterification reaction should not be stored for a longer time. Since due to prolonged storage alcohols in general get acidic this inter will affect the yield of transesterification.
3. Most importantly a great effort has to be put on getting an efficient way of phase separation. This could be achieved firstly by performing a perfect neutralization of catalyst using another inorganic acid. And secondly by finding an efficient and effective way of ethanol recovery system. One thing I could recommend for the later one is to use a vacuum distillation system. If a vacuum distillation system is employed, it will be possible to distillate the excess ethanol from the transesterified mixture using a much lower temperature. This intern eliminates the saponification problem and of course minimizes the energy consumption.

More over this study was only concentrated on the production optimization of biodiesel from Jatropha curcas oil with alcohol ethanol taking in to account only the effect reaction temperature and ethanol to oil molar ratio on ethanolysis yield and determining selected physicochemical properties of the biodiesels. For better understanding of the biodiesel production and to determine the optimum production parameters the transesterification reaction kinetics at different reaction parameters such as catalyst concentration and reaction time should be studied in detail. All the physicochemical properties of the biodiesel that determines the quality should be analyzed.

Finally product quality is the major factor that determines the widespread use of biodiesel fuel, especially for local production and use. Therefore it is essential to establish the product quality standardization, applicable to the country, which agrees with the internationally accepted standard specifications as ASTM and EN.

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APPENDIX

A. Tables

Table A-1 World Top 20 Biodiesel Producing Countries (Million of Liters/year)

Country	**Years**				
	2005	2006	2007	2008	2009
Germany	2263.18	4085.34	4543.78	3580.47	2971.15
France	487.46	673.15	1085.17	1996.24	2385.05
United States	343.66	948.02	1854.19	2559.90	1911.09
Italy	446.83	673.15	533.88	760.20	760.20
Brazil	0.74	69.00	404.33	1163.94	1608.05
Argentina	11.61	34.82	435.23	887.86	1340.50
Spain	185.70	69.64	191.50	249.53	638.33
China	46.42	232.12	348.18	464.24	464.24
Austria	92.85	139.27	301.76	243.73	353.99
Thailand	23.21	23.21	69.64	446.83	609.32
Czech Republic	143.92	127.67	92.85	87.05	175.83
Belgium	1.16	28.43	185.70	313.36	470.05
Poland	69.64	104.45	52.23	290.15	388.80
United Kingdom	52.23	220.52	168.29	214.71	156.68
Malaysia	0.00	63.83	145.08	261.14	330.77
Portugal	1.16	104.45	203.11	179.89	284.35
Denmark	81.24	81.24	81.24	104.45	104.45
Korea, South	11.61	52.23	98.65	185.70	290.15
Slovakia	87.05	92.85	52.23	162.49	116.06
Netherlands	0.00	20.31	98.65	116.06	313.36

Source: US Energy Information Administration Independent Statistics and Analysis

http://tonto.eia.doe.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=79&pid=79&aid=1

Table A-2 World Top 20 Biodiesel Consuming Countries (Million of Liters/year)

Country	**Years**				
	2005	2006	2007	2008	2009
Germany	2263.18	4004.10	4520.57	3429.59	2971.15
France	413.18	783.41	1468.17	2356.03	2640.38
United States	343.82	986.42	1355.77	1192.15	1192.90
Brazil	3.48	63.83	370.23	1108.38	1564.93
Italy	226.32	255.33	232.12	806.62	1346.30
United Kingdom	34.82	168.29	348.18	882.06	986.52
Spain	185.70	69.64	342.38	667.35	1149.00
Austria	98.65	319.17	359.79	353.99	441.03
China	46.42	232.12	348.18	464.24	464.24
Thailand	5.80	5.80	63.83	446.83	609.32
Poland	17.41	52.23	29.02	388.80	504.86
Netherlands	2.90	28.43	284.35	230.38	295.95
Portugal	0.17	92.85	174.09	162.49	295.95
Korea, South	11.61	52.23	98.65	185.70	290.15
Sweden	11.61	58.03	127.67	162.49	174.09
Belgium	0.00	1.16	116.06	110.26	290.15
Eurasia	11.61	20.54	56.35	180.47	190.34
Colombia	0.00	0.00	5.80	81.24	319.17
Romania	0.00	29.02	52.23	150.88	168.29
Canada	11.61	46.42	92.85	98.65	105.03

Source: US Energy Information Administration Independent Statistics and Analysis.

http://tonto.eia.doe.gov/cfapps/ipdbproject/IEDIndex3.cfm?tid=79&pid=79&aid=1

Table A-3 Ethiopian Gasoil Import per Metric ton Price in USD

Months	**Years**										
	1999 / 2000	2000 / 2001	2001 / 2002	2002 / 2003	2003 / 2004	2004 / 2005	2005 / 2006	2006 / 2007	2007 / 2008	2008 / 2009	2009 / 2010
Jul	147.56	306.51	214.14	211.26	224.46	335.74	520.31	651.37	645.94	1259.91	557.47
Aug	161.17	261.89	216.14	213.49	236.91	374.66	529.21	645.03	624.39	1004.12	615.37
Sep	174.41	299.23	222.92	233.76	237.68	393.04	555.42	568.27	684.44	902.60	580.46
Oct	178.38	287.49	192.87	236.62	245.50	418.01	528.33	539.33	718.76	636.25	616.94
Nov	185.45	253.80	16.97	221.87	255.36	396.48	509.26	533.84	806.41	531.06	651.36
Dec	192.26	229.86	158.39	234.28	263.21	353.68	470.69	529.54	789.12	460.53	627.90
Jan	215.79	199.09	165.41	242.30	294.31	356.94	328.34	498.12	789.05	461.24	649.18
Feb	215.06	192.85	170.00	280.69	277.67	390.48	493.76	535.01	835.10	387.70	636.54
Mar	248.32	195.28	193.58	247.83	277.26	462.97	544.70	554.15	946.58	415.47	678.52
Apr	190.94	223.82	216.09	209.35	287.49	474.62	465.73	606.13	1038.47	464.82	730.54
May	197.96	232.06	218.02	205.15	329.54	437.83	433.56	615.73	1186.77	507.79	677.08
Jun	219.31	223.45	213.04	211.78	308.79	488.29	639.65	617.97	1232.49	595.67	662.75
Average	193.88	242.11	183.13	229.03	269.85	406.90	501.58	574.54	858.13	635.60	640.34

Source: Ethiopian Petroleum Enterprise

Table A-4 Ethiopian Gasoil Import Quantity from 1999 to 2010 in 10^3 MT

Months	Years										
	1999 / 2000	2000 / 2001	2001 / 2002	2002 / 2003	2003 / 2004	2004 / 2005	2005 / 2006	2006 / 2007	2007 / 2008	2008 / 2009	2009 / 2010
Jul	63.82	34.04	62.12	59.73	59.51	72.40	58.04	81.52	64.55	97.55	109.73
Aug	55.62	42.54	54.65	35.50	70.08	42.89	62.69	73.34	88.16	100.06	100.65
Sep	13.50	87.43	33.61	56.47	47.94	69.00	38.37	57.73	72.78	84.34	94.17
Oct	36.97	54.28	32.63	68.09	35.97	48.17	55.59	67.18	67.65	71.89	129.64
Nov	37.99	32.18	83.55	57.75	54.25	37.70	74.32	57.99	93.10	87.72	86.36
Dec	68.53	48.15	60.97	62.91	44.68	93.84	71.34	89.72	96.91	99.83	107.89
Jan	30.22	72.99	42.70	45.92	59.13	68.96	80.78	87.40	102.85	90.39	102.66
Feb	44.72	45.87	57.60	65.99	76.29	61.95	66.53	91.08	102.60	114.51	61.93
Mar	69.59	49.61	35.04	67.99	72.50	59.83	72.95	80.30	85.65	103.88	127.81
Apr	46.70	54.00	58.35	65.97	57.72	68.79	91.65	68.17	109.82	128.52	117.79
May	21.83	34.41	60.88	65.97	50.35	49.04	63.83	85.17	80.75	111.21	99.60
Jun	59.31	55.35	41.07	26.99	60.09	100.68	75.60	65.88	108.34	113.68	99.69
Total	548.79	610.83	623.20	679.28	688.53	773.26	811.69	905.48	1073.15	1203.57	1237.92

Source: Ethiopian Petroleum Enterprise

Table A-5 Summary of transesterification yield

Rank	Temp [ºC]	Molar Ratio	NaOH Conce.	Yield	Specific gravity	Viscosity [mm^2/s]
1	70	9:01	1.50%	80.00	0.86	4.13
2	55	6:01	1.50%	64.33	0.86	4.01
3	70	6:01	1.50%	55.00	0.86	4.40
4	70	8:01	1.50%	55.00	0.86	4.21
5	65	6:01	1.50%	53.00	0.86	4.09
6	70	7:01	1.50%	51.67	0.86	4.03
7	55	8:01	1.50%	51.25	0.86	4.07
8	65	8:01	1.50%	49.00	0.86	4.45
9	78	6:01	1.50%	47.67	0.86	4.28
10	78	8:01	1.50%	46.88	0.86	4.26
11	55	9:01	1.50%	46.00	0.86	4.15
12	55	7:01	1.50%	44.67	0.86	4.38
13	65	9:01	1.50%	43.75	0.86	4.05
14	78	9:01	1.50%	41.00	0.86	4.42
15	65	7:01	1.50%	40.67	0.86	4.43
16	78	7:01	1.50%	40.30	0.86	4.17

Table A-6 Effect of ethanol to oil molar ratio on yield, density, and viscosity

MR	**Temp [°C]**	**Yield**	**Specific gravity**	**Viscosity [mm^2/s]**
6:1	55	64.33	0.86	4.01
	65	53.00	0.86	4.09
	70	55.00	0.86	4.40
	78	47.67	0.86	4.07
7:1	55	44.67	0.86	4.13
	65	40.67	0.86	4.43
	70	51.67	0.86	4.38
	78	40.30	0.86	4.17
8:1	55	51.25	0.86	4.43
	65	49.00	0.86	4.21
	70	55.00	0.86	4.28
	78	46.88	0.86	4.45
9:1	55	46.00	0.86	4.26
	65	43.75	0.86	4.15
	70	80.00	0.86	4.13
	78	41.00	0.86	4.42

Table A-7 Effect of reaction temperature on yield, density, and viscosity

Temp	**MR**	**Temp [ºC]**	**Yield**	**Specific gravity**	**Viscosity [mm^2/s]**
55	6:1	64.33	57.70	0.86	4.01
	7:1	44.67	38.00	0.86	4.38
	8:1	51.25	46.30	0.86	4.43
	9:1	46.00	41.00	0.86	4.26
65	6:01	53.00	46.30	0.86	4.09
	7:01	40.67	34.00	0.86	4.43
	8:01	49.00	44.00	0.86	4.21
	9:01	43.75	38.80	0.86	4.15
70	6:01	55.00	50.00	0.86	4.09
	7:01	51.67	45.00	0.86	4.38
	8:01	55.00	50.00	0.86	4.28
	9:01	80.00	75.00	0.86	4.13
78	6:01	47.67	41.00	0.86	4.07
	7:01	40.30	33.70	0.86	4.17
	8:01	46.88	40.90	0.86	4.45
	9:01	41.00	36.00	0.86	4.42

$CH2_2O$