Selection of seed oil biodiesel producing tree species, emission reduction and land suitability

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Abstract: Biodiesel is a renewable fuel, highly demanded globally at the beginning of the 21st Century because of depletion of fossil fuel reserve and environmental issues. In this paper, oil yielding tree species were reviewed and seeds of nine tree species were collected to select best seed oil producer and its emission reducing biodiesel and land suitability. Seed oil was extracted by mechanical, hydraulic and chemical methods and stored at room temperature (25°C) and deep freeze (–20°C). Then, the tree species with highest oil yield was further studied its biodiesel, estimated end use emission as rural household energy and its land suitability. Using hexane solvent, the oil yield was 12 (%, w/w) in *Cordia africana* to 50.2 (%, w/w) in *Croton megalocarpus,* which was 44.7% in hydraulic seed oil press. The biodiesel yield of *C. megalocarpus* was 82% to 100% (w/w), calorific value 38.8 to 43.2 MJ kg^{-1}, and flashpoint to 103°C. The biodiesel of *C. megalocarpus* contained esters like Octanoic acid methyl ester; and 9,12-Octadecadienoic acid (Z, Z)-, methyl esters. If a rural household uses biodiesel instead of firewood and kerosene, it is possible to reduce end use emission by 38.9% to 39.4%. As *C. megalocarpus* is a multipurpose tree species with potential source of cooking biodiesel fuel, it can be planted in some 34 million ha suitable land areas of Ethiopia.

Keywords: *Croton megalocarpus*, land suitability, end use emission, seed oil extraction

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1 Introduction

Biodiesel received attention in 21st Century as cleaner and environmentally safe, renewable and biodegradable fuel, because of fossil fuels' depletion of reserve, and price fluctuation (Liaquat et al., 2010). Although vegetable oil is a source of energy in motor engines, it needs to be converted to light biodiesel that meets the standards of American Society for Testing and Materials (ASTM) D6751 (Knothe, 2009). Vegetable oils, tri-glycerides of fatty acids, are esters of fatty acids that have high density (≥800 kg m^{-3}) and high viscosity. In transesterification, fatty acid triglycerides are catalyzed to react with short chain alcohols to produce glycerol and biodiesel, fatty acid methyl ester (FAME) (Anastopoulos et al., 2009; Upadhyay and Sharma, 2013). The conversion of seed oils to FAME (Figure 1) requires raw oil, 15% (w/w) methanol and 5% sodium hydroxide, or molar ratios of methanol to oil 3 to 12 (3:1 to 12:1) and catalyst ≥1% (Ahmad et al., 2011). The alkyl groups (R) in triacylglyceride (fat or oil) (Figure 1) could be similar or different.

Biodiesel quality determination follows ASTM 6751 and European's EN14214 standards including fatty acid types, iodine value, saponification value, flash point, cetane number and others (Tariq et al., 2015). There are over 1000 fatty acids in fats and oils including palmitic (hexadecanoic_C16:0), stearic (octadecanoic_C18:0), oleic (octadecenoic_C18:1), linoleic (octadecadienoic_C18:2) and linolenic acids (octadecatrienoic_C18:3) (Knothe, 2009). The fatty acid

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composition of vegetable oils and corresponding esters depend on geographic location, harvesting period and intervals, genotypes, fertilization regimes, environment, analytical conditions and subsequent handling (Najafi et al., 2011; Sakar et al., 2014). Contaminants of biodiesel include unreacted Triacylglyceride (TAG) and unseparated glycerol that create engine filter clogging, or fuel deterioration. Biodiesel has lower volumetric energy content than petroleum diesel (Alnuami et al., 2014) depending on the esters (Oliveira and Da Silva, 2013). The biodiesel esters are recently identified by Gas Chromatography Mass Spectrometry (GC-MS) (Gerpen, 2004), aided by National Institute of Standards and Technology Library (NIST).

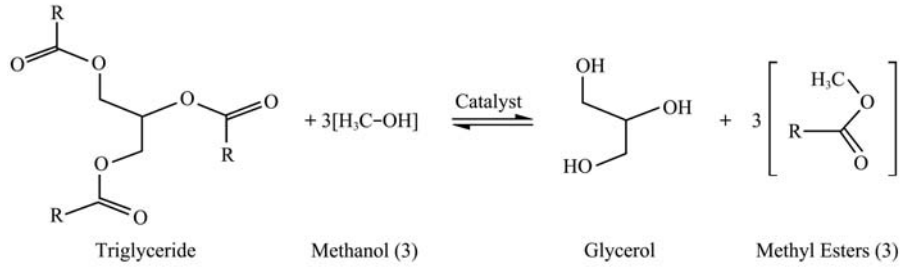


Figure 1 Transesterification, of seed oil to biodiesel with methanol (Ahmad et al., 2011)

Biodiesel reduces 86% of carbonaceous greenhouse gases emission but increases NO_X emission compared to petro diesel (Table 1) (Depcik et al., 2015). The use of biodiesel reduces the emission of carcinogens and polycyclic aromatic hydrocarbons (PAHs) in the exhaust gas (El Bassam, 2010).

Table 1 Comparison of emissions from biodiesel and petro diesel (Depcik et al., 2015)

Fuel	CO (g kg^{-1})	Total HC (g kg^{-1})	NO_X (g kg^{-1})	Particles (g kg^{-1})
Diesel	0.634	0.146	0.986	0.083
B20	0.574	0.128	0.991	0.078
B100	0.497	0.058	1.025	0.072

Since biodiesel production from edibles oils is expensive, searching non-edible vegetable oil sources like trees become important (Atabani et al., 2013). Mass production, better energy efficiency and reduced viscosity made tree based oil production preferable to annual crops (Kartha, 2006). From the 3000 plant species frequently used globally, 280 contain oil in seeds, fruits, tubers and/ or roots (El Bassam, 2010). In Ethiopia, 5% biodiesel blend was planned to replace 0.28 billion liter diesel in 2030 (CRGE, 2011). However, *Jatropha, Palm, Caster bean* etc. to be used for biodiesel production faced various problems like land suitability (Portner, 2013). Thus, sustainable production of biodiesel from nonedible oil producing plants species need to be diversified on suitable lands (Atabani et al., 2013).

Rural households in Ethiopia have smoky cooking biomass energy. However, biodiesel has low indoor pollution that can be made and used in rural houses as alternative cooking energy (Bob and Estill, 2015). Seed oil extraction methods dominantly are chemical solvents like hexane (Santos et al., 2013) that produces higher seed oil than the rural place's accessible manual or hydraulic seed oil press. However, chemical solvents consume greater energy than the expeller and releases volatile organic compounds that affect environment and human health (Pighinelli and Gambetta, 2012). The objective of this study was to select greatest seed oil producing tree species and compare the quantity and quality of seed oil and biodiesel of the greatest oil yielding tree under different extraction methods and determine the end use emission and land suitability of the selected oil producer.

2 Material and methods

2.1 Selection of plant species

Oil yielding tree species were reviewed and nine tree species were selected in turn to select the greatest seed oil producer from list. *Bersama abyssinica* Fresen., *Croton megalocarpus* Hutch., *Jatropha curcas* L., *Ximenia americana* L., *Vepris dainelii* (Pichi-Serm), *Ziziphus mucronata* Willd., *Phoenix reclinata* Jacq., *Cordia africana* Lam. and *Podocarpus falcatus* (Thunb.) R.Br. ex Mirb. which are described in Bekele (2007), Verma (2009), Aliyu et al. (2010), Kibazohi and Sangwan (2011), Dereje and Desalegn (2013), and Mathewos et al. (2015) were mostly obtained from

Enemorina Ener district, but *Croton* from Hawassa city and *Vepris* from Arba Minch in Southern Ethiopia.

2.2 Methods of seed collection, oil extraction and storage

Composite seed samples were collected from 20-25 representative matured trees of the nine species (FAO, 1975). The fruits of all the species were manually decorticated to remove the hard outer shells. Seeds dried under shade for 1 to 3 days, seed coats removed, seeds cleaned and ground based on the type of species. The number of seeds were determined by 1000 seed weight (ISTA, 2003). Then dried seeds of *B. abyssinica*, *C. megalocarpus* and *V. dainelii* was ground by mortar steel electric mill and that of *J. curcas*, *P. falcatus*, and others by manual grinder. The ground seeds were sieved by 1-2 mm sieve, weighed with sensitive balance (Adam Lab.equip. Leic. LE67FT-England, 0.0001 g), packed in plastic tube and kept in deep freeze (–20°C) for a month till oil extraction. For chemical solvent oil extraction, 250 mL hexane and 60 g crushed seed was put in soxhlet extractor on heating mantel at 60°C-65°C for 150 minutes in triplicates and the amount of oil yield was determined for all species.

Mechanical and hydraulic seed oil press (50 ton) were additionally used to extract seed oil from *C. megalocarpus* (Figure 2) and stored for a month in deep freeze (–20°C) till transesterification. The oil and biodiesel of *C. megalocarpus* was characterized at three extraction methods (hexane solvent, mechanical press and hydraulic press). Mechanically pressed seed oil was stored at 25°C and –20°C.

(a) Manual mechanical seed oil press (b) Hydraulic seed oil press (50 tonnes) (c) Solvent (soxhlet) seed oil extractor

Figure 2 Materials for seed oil extraction methods (a-c)

2.3 Determination of physico-chemical properties of *C. megalocarpus* seed oil

The oil of *C. megalocarpus* was degummed by mixing with 3% (v/v) distilled water and 1.5% (v/v) orthophosphoric acid, and stirred for an hour at 70°C. Impurities were removed by centrifuging at 2000 rpm for 20 minutes. Moisture content of triplicated 5 g oil and crushed seed was determined by drying at 105°C to constant weight (Equation 1). pH was measured by standardized buffer solution, 3505 pH meter at 25°C. Density of oil at 30°C-40°C was determined by direct measurement of mass to volume ratio. Ash content of oil was determined by burning 5 g oil in furnace at 600°C for 4 hours (AOAC, 2000) (Equation (2)).

2.3.1 Acid value and free fatty acid

In 1000 mL conical flask 0.1 N ethanolic KOH (99.5% ethanol) was prepared, filtered and stored for 24 hours in dark bottle. About 2.5 g oil was dissolved in a mixture of 95% ethanol (25 mL) and diethyl ether (25 mL) solution (Gerpen, 2004). The solution was titrated with 0.1 N ethanolic KOH solution in the presence of pipetted 5 drops of phenolphthalein till colorless to faint pink color that persisted for ≥30 seconds (Equation 3). Free fatty acid (FFA) was determined from acid value (Equation (4)). Then the oil was neutralized by common salt (Equation (5)).

2.3.2 Saponification value

About 2 g oil was dissolved in 25 mL ethanolic KOH solution (0.5N KOH in anhydrous ethanol (99.8%, w/w) and refluxed for 30 minutes on a magnetic stirrer at 70°C, where left to cool and added 5 drops of phenolphthalein indicator. Then hot soap solution obtained was slowly titrated with 0.5N HCl acid solution in distilled water (*Va*) till pink to red color (Nayak and Patel, 2010) in sample

and blank (*Vb*) (Equation (6)).

2.3.3 Iodine absorption

In 500 mL conical flask, 0.25 g oil, 10 mL chloroform and 25 mL Hanus iodine solution were added, shaken and left to stand in the dark for 30 minutes. Then 10 mL KI (15%) was added and shaken thoroughly and rinsed by 100 mL distilled water for the sample and blank (AOAC, 2000). The solution was titrated with 0.01 N thiosulfate solution using 1 mL starch to get fade color (Equation (7)).

2.4 Characterization of *C. megalocarpus biodiesel*

Transesterification was done by adding 6 to 1, methanol to seed oil in molar ratio, 1% (w/w) NaOH and then refluxed for 1 hr at 65°C. The glycerol and biodiesel (Figure 3) were separated by settling for 12 hrs in separatory funnel (Gerpen, 2004).

Figure 3 Biodiesel separation from glycerol (right side)

The biodiesel was purified by washing with excess warm tap water and dried by heating at 105°C for 6 hours. Calorific value was determined by adiabatic bomb calorimeter (Parr® Adiabatic Calorimeter, 115 V, 50 Hz, 2.0 Amps, Parr instr. Comp.) for 1 g sample using oxygen filled bomb at 30 atm. Flash point was determined by Pensky Martins Flash Point Cup Apparatus (DM93). Cetane number was estimated by formula (Equation (8)).

2.4.1 Analysis of fatty acids

Fatty acid esters of *C. megalocarpus* biodiesel was analyzed by GC-MS (Agilent Tech. 7890A GC system with 5975c inert MS9 &Triple Axis Detector) equipped with GC column (HP-5MS, 30 m×250 μm×0.25 μm). Sample of 1 μL biodiesel was injected at 50°C. The temperature was maintained 50°C for 2 minutes, then at 5°C minutes^{-1} to 250°C held for 5 minutes, using helium a carrier gas at 1 mL minute^{-1} constant flow. The GC-MS interface temperature was set to 232°C and electron ionization (EI) 70 ev energy. Spectral data were referred to an inbuilt library of NIST and chemstation software.

2.4.2 Biodiesel in reducing end use emission in comparison with firewood and kerosene

Emission of the three common GHG was determined using lower heating value (LHV) of the fuel. LHV of firewood and liquid fuel was 80% and 95% of their higher heating value (HHV), respectively (Forest Products Laboratory, 2004). The emissions were converted to carbon dioxide equivalent (CO_2^{-e}) (Table 2) by considering the daily energy consumption of rural households in three agroecological zones of Enemorina Ener district, lowland 500-1600 m; midland 1600-2400 m; and highland 2400-3200 m for common firewood species *Dodonea angustifolia* (HHV: 18.14 MJ kg^{-1}), *Eucalyptus camaldulensis* (HHV: 18.06 MJ kg^{-1}) and *E. globulus* (HHV: 19.28 MJ kg^{-1}) firewood species, respectively. Although emissions of fuels exist throughout the life cycles, the concern of indoor pollution reduction was end use emission. IPCC **(**2006) default emission factor was used to determine the end use emission of firewood (Equation (9)) and biodiesel (Equation (10)).

Table 2 Emission factors and global warming potential of three common GHG (IPCC, 2006; IPCC, 2001)

Type of GHG	Residential source, stationary, Gas Emission Factor		GWP (100 yr time horizon)
	Firewood (kg TJ^{-1})	Biodiesel (kg TJ^{-1})	
CO_2	112000	70800	1
CH_4	210	10	23
N_2O	4	0.6	296

2.5 Land suitability analysis for *C. megalocarpus*

Suitable land area was mapped using Arc GIS 10.3 from suitable site requirements of *C. megalocarpus* documented elsewhere. The suitable sites were with altitude 700-2300 m above sea level, annual temperature 11-30°C, annual rainfall 800-1900 mm, sandy loam soil, pH 3.0-8.99 and soil depth ≥50 cm in its native region in semi- arid and sub humid Tropical East Africa (Bolza and Keating, 1972; Maundu and Tengnäs, 2005). The site requirements were transformed in to common scale (Nyebenge et al., 2009) and overlaid on the whole Ethiopia regardless of the existing land uses.

2.5.1 Statistical analyses

All the data were statistically analyzed for mean, standard error and Pearson's correlation using SPSS

version 16 and excel spread sheet 2016.

$$Moisture\ content\ (\%) = \frac{Initial\ weight\ (\mathrm{g}) - Oven\ dried\ weight\ (\mathrm{g})}{Initial\ weight\ (\mathrm{g})} \times 100 \quad (1)$$

$$Ash\ content\ of\ oil\ (\%) = \frac{Weight\ of\ ash\ (\mathrm{g})}{Weight\ of\ oil\ sample\ (\mathrm{g})} \times 100 \quad (2)$$

$$Acid\ Value\ (AV) = \left(\frac{mg\ KOH}{g}\right) = \frac{56.1 \times (Vs - Vb) \times N}{w} \quad (3)$$

where, *Vs* is volume of sample (mL) and *Vb* is volume of blank of 0.1 N ethanolic KOH solution (mL); *N* is concentration of ethanolic KOH; *w* is weight of oil (g).

$$Free\ Fatty\ Acid\ (FFA)\ (\%) = \frac{AV}{2} \quad (4)$$

where, *AV* is acid value in % (Gerpen, 2004).

2.5.2 Neutralization of oil

The presence of excess free fatty acid (FFA) was neutralized by adding NaOH. The mass (m) of NaOH required to neutralize the FFA (Table 3) was determined as Equation (5).

$$R - COOH - CH + NaOH \rightarrow R - COONa + H_2O$$

$$m(NaOH) = \frac{(\%FFA) \times M(NaOH)}{M(FFA)} \quad (5)$$

where, "*m*" is mass of NaOH for neutralization (g); *FFA* is free fatty acid (%); *M*(*NaOH*) is molecular weight of NaOH (g) and *M*(*FFA*) is the molecular weight of Free Fatty Acid (g).

Table 3 Neutralization of different free fatty acids of *C. megalocarpus* seed oil

Type of extraction & storage temperature	Hexane & –20°C	Mechanical & 25°C	Hydraulic & –20°C	Mechanical & –20°C
Acid Value (AV)	2.15	3.82	5.01	2.94
FFA%	1.08	1.91	2.51	1.47
$^1M_{(FFA)}$ (g)	305.92	294.19	294.11	279.81
$^1M_{(NaOH)}$ (g)	40.0	40.0	40.0	40.0
$^2m_{(NaOH/g\ oil)}$ (g)	0.0014	0.0026	0.0034	0.0021

Note: ^{1}M: molecular weight; ^{2}m: required mass.

$$Saponification\ value\ (SV) = \left(\frac{mgKOH}{g}\right) = \frac{56.1 \times N \times (V_{bh} - V_a)}{w} \quad (6)$$

where, V_{bh} is volume of HCl required for the blank (mL); V_a is volume HCl required for the sample (mL); *N* is Normality of the standard HCl; *w* is weight of oil sample (g) and 56.1 is molecular weight of KOH (g).

$$Iodine\ absorption\ value\ (\mathrm{g\ I_2\ 100\ g^{-1}}) = \frac{(B - S) \times N \times 12.69}{w} \quad (7)$$

where, *B* is volume of standard thiosulfate required for the blank (mL); *S* is volume of standard thiosulfate required for the sample (mL); *N* is Normality of the standard thiosulfate solution; *w* is weight of oil sample (g); 12.69 is molecular weight of iodine used to convert from mEq thiosulfate to I.

$$CN = 46.3 + \left(\frac{5458}{Sn}\right) - (0.225 \times IV) \quad (8)$$

where, *CN* is Cetane Number (unit less); *Sn* is saponification value of sample (mg KOH g^{-1}); *IV* is Iodine Value of sample (g I_2 100 g^{-1}) (Jesikha, 2012).

$$Wd\ em. = \sum_i^k Wd.\ cons._{(ijk)} \times EF_{(ijk)} \times GWP_{(ijk)} \quad (9)$$

$$Bdl\ em. = \sum_i^k Bdl.\ cons._{(ijk)} \times EF_{(ijk)} \times GWP_{(ijk)} \quad (10)$$

where, *Wd em.* is emission from firewood (kg CO_2^{e-}); *Bdl em.* is emission from biodiesel (kg CO_2^{e-}); *EF* is emission factor in net calorific value (kg TJ^{-1}); *GWP* is Global warming potential of a given gas at 100 years' time horizon (Table 3); *Wd* cons. is Wood consumption (TJ kg^{-1}); *Bdl cons.* is biodiesel consumption (TJ kg^{-1}); *i* is CO_2; *j* is CH_4 and *k* is N_2O.

3 Results

3.1 Characteristics of seeds and extraction of seed oil of different tree species

The big sized seeds like *J. curcas* and *C. megalocarpus* were manually hammered to remove hard fruit pod and seed coat. Small seeds with fleshy coat like *V. dainelii* and *Z. mucronata* were hand shaken and washed to remove fruit pod manually. There were 3-5 seeds per fruit pod and 450-8000 seeds in a kilogram of fruit pod. The number of seeds ranged from 4300 seeds (*C. africana*) to 1400 seeds (*V. dainelii*) (Table 4).

For oil extraction, different size reduction method was used for example, manual grinding was used in seeds like *J. curcas* and *P. falcatus* because of better oil content, which was made difficult grinding by mortar electric grinding mill. The oil yield ranged from 12 % (w/w) in *C. africana* to 50.2% (w/w) in *C. megalocarpus* (Figure 4) at

moisture level of 5.1% to 6.7% (w/w). As the number of seeds per fruit pod increased, the number of seeds per kg also increased (p<0.01). However, there was no significant correlation between seed number and oil yield (Table 5). The negative correlation of oil yield with seed or fruit number per kilogram could be attributed to few numbers, but larger sized seeds produce greater oil.

Table 4 Mean number of seeds in a kilogram of seeds and fruits of different species

Species	No. of seeds/kg	No. of seeds/ fruit pod	No. of seeds/ kg fruit pod
B. abyssinica	2230	3-5	550
J. curcas	2350	3-4	450
C. megalocarpus	2100	3-5	500
X. americana	1500	3	750
Z. mucronata	2650	3-4	1300
V. dainelii	1400	1	1400
P. reclinata	1600	1	1600
C. africana	4300	4-6	8000
P. falcatus	1600	1	900

Note: *Washing was done using potable tap-water unless otherwise specified.

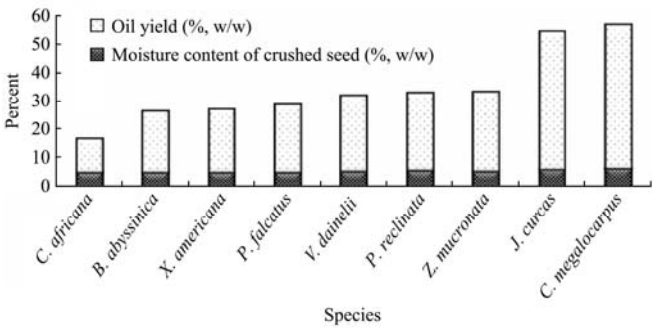


Figure 4 Seed oil yield and moisture content of different tree species

Table 5 Pearsons' correlation matrix of seed characteristics and oil yield

	No. of seeds kg^{-1}	No. of seed/fruit pod	Weight of the No. of seeds kg^{-1} fruit pod	Oil yield in hexane solvent (%, w/w)
Species	0.072	–0.422	0.513	–0.52
No. of seeds kg^{-1}		0.813**	0.802**	–0.184
No. of seed/fruit pod			0.467	–0.098
No. of seeds kg^{-1} fruit pod				–0.574

Note: No. =number; **. Correlation is significant at P<0.01.

3.2 Characteristics of *C. megalocarpus* seed oil under three extraction methods

Degummed seed oil samples in hexane extraction method was visually transparent more than the other extraction methods. The maximum seed oil yield of *C. megalocarpus* was obtained by hexane solvent (50.2%), followed by hydraulic seed oil press (44.67%) (Table 6). The highest moisture content of oil (2.516%) was obtained from hexane extraction and the lowest (0.252%) from mechanical press (Table 7) for the same seed sample of 5.85% moisture (Table 6).

Table 6 Seed oil yield, time taken and moisture of *C. megalocarpus* in three extraction methods

Extraction methods	Oil yield (%, w/w)	Time taken in extraction (minutes)	Moisture content of grounded seed (%, w/w)
Soxhlet chemical hexane solvent	50.2	150	5.85
Mechanical press	29.6	90	5.85
Hydraulic press (50 tonnes capacity)	44.67	50	5.85

Table 7 Characteristics of *C. megalocarpus* seed oil under three extraction methods

Characteristics/Type of extraction & storage temperature	Mean ±Std. error				
	Moisture content (%, w/w)	Density (g cm^{-3}) (30-40°C)	Acid value (mg KOH g^{-1})	Saponification value (mg KOH g^{-1})	Iodine value (g I_2 100 g^{-1})
Hexane & –20°C	2.52±0.5^{b}	0.91±0.04^{a}	2.15±0.14^{c}	166.08±1.64^{a}	117.51±0.25^{a}
Mechanical & 25°C	0.24±0.1^{a}	0.89±0.02^{a}	3.82±0.41^{b}	199.42±3.38^{b}	116.49±0.25^{a}
Hydraulic & –20°C	0.25±0.1^{a}	0.88±0.02^{a}	5.01±0.32^{a}	187.12±11.12^{ab}	112.43±5.33^{a}
Mechanical & –20°C	0.57±0.002^{a}	0.90±0.44^{a}	2.94±0.31^{bc}	178.61±4.41^{ab}	116.75±1.52^{a}

Note: a, b and c are significant at p<0.05.

The density of *C. megalocarpus* oil produced at the three methods of extraction was 0.88 to 0.91 g cm^{-3} but did not vary significantly (Table 7). Hydraulic press resulted in highest acid value (5.011%±0.319%) probably because of the iron and dust particles. Mechanically pressed, room temperature stored seed oil was highest in saponification value of 199.42±3.382 (mg KOH g^{-1} oil) which indicated the presence of more free fatty acids (Table 7).

3.3 Biodiesel of *C. megalocarpus* seed oil

The highest biodiesel yield about 100% (v/v) was obtained in hexane extracted seed oil but the lowest about 82% (v/v) in hydraulic pressed seed oil (Table 8), probably because of contaminants in the latter press. The mechanically pressed, deep freeze stored biodiesel was preferable because of 43.2 MJ kg^{-1} calorific value and 137°C flash point (Table 9). The biodiesel was sufficiently burnt without smoke and it can be used for

rural household cooking (Figure 5). The cetane number of biodiesel was 65.87 to 72.4 (Table 9) was negatively correlated with saponification value. The calorific value of the biodiesel was also negatively correlated with the iodine number (p<0.01) (Table 10), because the existence of greater number of double bonds is not preferred for energy purpose.

Table 8 Yield and density of biodiesel and glycerol of *C. megalocarpus* seed oil in three extraction methods

Oil extraction method & storage temperature	Yield (%, v/v) (at 30-40°C),		Density (g cm^{-3}) (at 30-40°C)	
	Biodiesel	Glycerol	Biodiesel	Glycerol
Hexane & –20°C	100.0	61.7	0.889	0.990
Mechanical & 25°C	93.3	48.7	0.874	0.995
Hydraulic & –20°C	82.0	60.0	0.849	0.933
Mechanical & –20°C	94.0	49.0	0.892	0.956

Table 9 Physicochemical properties of *C. megalocarpus* biodiesel in comparison to petro diesel

Type of extraction and storage/properties	Mechanical & –20°C	Mechanical & 25°C	Hydraulic & –20°C	Hexane & –20°C	Petro- diesel*	ASTM value
Moisture content (%, w/w)	0.563	0.582	0.568	0.601		
Density (40°C, g cm^{-3})	0.84	0.88	0.854	0.886	0.8231	N/A
Dynamic viscosity (40°C, mpa.s)	2.10	2.00	1.45	2.01		
Kinematic Viscosity (40°C, mm^2 s^{-1})	2.49	2.273	1.698	2.269	2.87	1.9-6.0
Acid value (mg KOH g^{-1})	0.802	0.829	0.845	0.68	ND	0.8 (max)
FFA (%, w/w)	0.401	0.414	0.423	0.34		
Saponification (mg KOH^{-1})	115.75±8.52	108.19±6.83	118.49±2.32	105.13±1.28		
Iodine value (g I_2 100 g^{-1})	114.11±5.57	116.01±4.85	117.76±2.21	114.74±3.32		
Calorific value (MJ kg^{-1})	43.19	39.97	38.81	40.47	44.65	-
Flash point (°C)	137	>200	-	103	65	130 (min.)
Cetane number	67.78	70.65	65.87	72.40		48-60
Ash content (%, w/w)	0.01	0.021	0.01	0.012		

Note: * Sources (Okoro et al., 2011).

Table 10 Correlation of some fuel characteristics of *C. megalocarpus* biodiesel

	Saponification (mg KOH g^{-1})	Iodine value (g I_2 100 g^{-1})	Calorific value (MJ kg^{-1})	Flash point (°C)	Cetane number
Acid value (mg KOH^{-1})	0.717	0.586	–0.186	0.77	–0.759
Saponification (mg KOH^{-1})		0.423	0.04	0.109	–.994**
Iodine value(g I_2 100 g^{-1})			–0.878*	0.416	–0.514
Calorific value (MJ kg^{-1})				–0.263	0.059
Flash point (°C)					–0.17

Note: **. Correlation is significant at P< 0.01 level; * at P<0.07 level.

Figure 5 Fueling lamp test of biodiesel of *C. megalocarpus*

3.4 Fatty acid composition of *C. megalocarpus* biodiesel

The esters identified in the biodiesel were dominantly unsaturated, about 1.3% (w/w) 13-Docosenoic acid, methyl ester, to 49.7% (w/w) Docosanoic acid, methyl ester. The number of esters found in mechanically pressed, room temperature stored oil biodiesel was greater than the others. Methyl hexadecanoate, Methyl-9-octadecenoate and Methyl-9,12 -octadecadienoate were well distributed (Table 11).

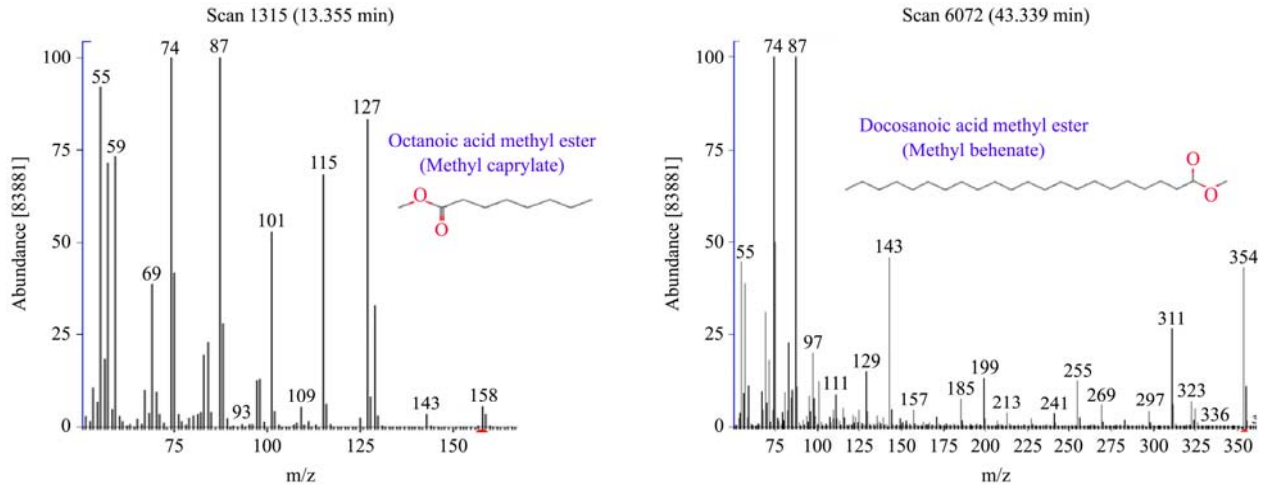
The mass fragmentation of the different fatty acids indicated the complexity of the composition, for example in Figure 6(a) parts of the ester, first 55 m z^{-1} separated then to 59, 69, 74 etc. were separated to full weight of ester called octanoic acid methyl ester molecular weight 158 m z^{-1}.

3.5 End use emission reduction of biodiesel

Using biodiesel of *C. megalocarpus* instead of firewood and kerosene at household could reduce end use emission indoor pollution by 38.90% to 39.42% (Table 12).

Table 11 Fatty acid methyl esters of *C. megalocarpus* biodiesel (%, w/w)

Type of extraction and storage/ systematic name	Chemical formula	Mechanical & –20°C	Mechanical & 25°C	Hydraulic & –20°C	Hexane & –20°C
Octanoic acid, methyl ester	$C_9H_{18}O_2$	37	13.6	15.4	6.1
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$		1.9		
9-Octadecenoic acid-, methyl ester	$C_{19}H_{36}O_2$			7.1	1.9
9,12-Octadecadienoic acid -, methylester	$C_{19}H_{34}O_2$	6.5	12.1		10.2
Methyl 9.cis.,11.trans.t,13.trans.-octadecatrienoate	$C_{19}H_{32}O_2$	26.7			
Eicosanoic acid, methyl ester	$C_{21}H_{42}O_2$	2.1	18.4	41.8	21.3
11-Eicosenoic acid, methyl ester	$C_{21}H_{40}O_2$		40.4	20.6	49.7
Docosanoic acid, methyl ester	$C_{23}H_{46}O_2$	11.2	3.3	6.1	1.7
13-Docosenoic acid, methyl ester,	$C_{21}H_{44}O_2$	7.3	1.3		



(a) Light ester compounds (b) Heavy ester compounds

Figure 6 Mass fragmentation of light and heavy ester compounds of *C.megalocarpus*

Table 12 Daily energy requirement and end use emission of gases in rural wooden houses

Fuel type in stove	Lowland		Midland		Highland	
	Daily energy LHV (MJ)*	End use emission kg CO_2^e	Daily energy LHV (MJ)	End use emission (kg CO_2^e)	Daily energy LHV (MJ)	End use emission (kg CO_2^e)
Firewood (conventional wood stove) with kerosene	105.62	12.46	74.61	8.80	53.10	6.27
Fire wood (conventional wood stove)	107.49	12.65	75.70	8.93	54.17	6.39
Biodiesel (stationary combustion)	107.49	7.65	75.90	5.40	54.57	3.89
Kerosene lamping (kerosene stove)	1.87	0.14	1.29	0.09	1.27	0.09
Biodiesel emission reduction from firewood &kerosene use (%, w/w)		39.42		39.26		38.90

Note: * (Converted from Miftah et al., 2017).

3.6 Growth and land suitability of *C. megalocarpus* in Ethiopia

At 2000 m elevation in Enemorina Ener district, Southern Ethiopia, the seeds of *C. megalocarpus* germinate 97% in 21 days and seedlings were grown 1.2 m within six months (Figure 7). Moreover, *C. megalocarpus* can grow in many parts of Ethiopia. Seeds can be obtained in Hawassa city, Ethiopia in February to March and about 34 million ha land area is identified to be suitable for its growth (Figure 8).

Figure 7 *C.megalocarpus* seedlings of six months' age

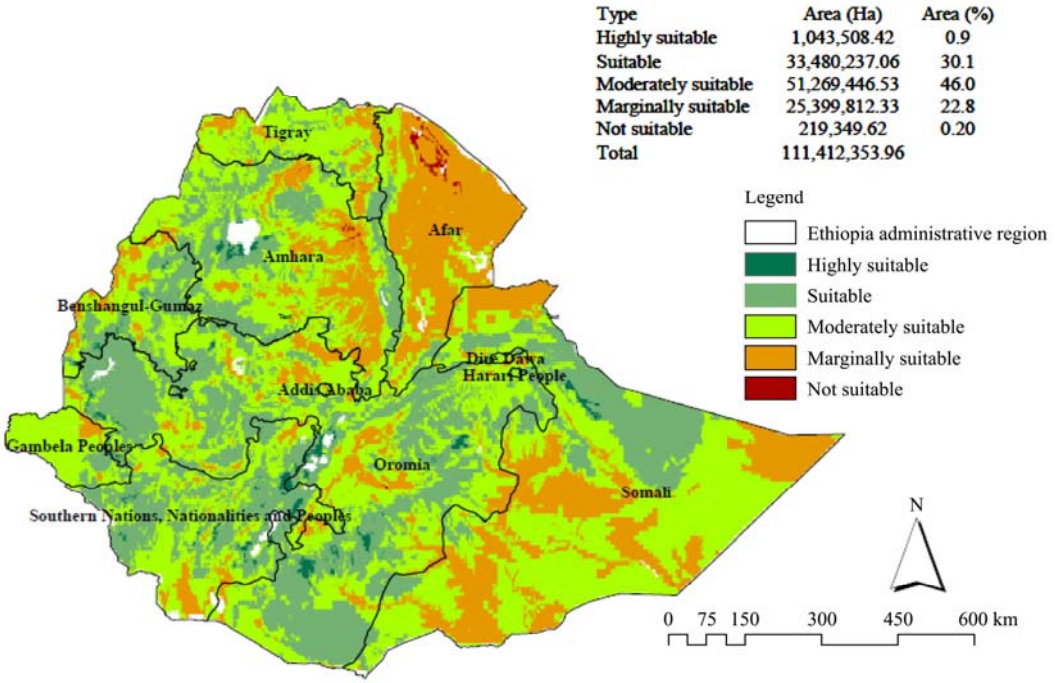


Figure 8 Land suitability of growing sites of *C. megalocarpus* in Ethiopia

4 Discussion

Oil producing tree species like *B. abyssinica, C. megalocarpus, X. americana, Z. mucronata, V. dainelii, P. reclinata, C. africana* and *P. falcatus,* were well distributed in different parts of Ethiopia and elsewhere (Bekele, 2007; Verma, 2009; Aliyu et al., 2010; Kibazohi and Sangwan, 2011; Dereje and Desalegn, 2013, and Mathewos et al., 2015). These species were underutilized; however, oil rich seeds can produce oil and biodiesel locally useful for lamps, stoves and generators, or turned into soap (Slingerland and Schut, 2014). Seeds with fleshy fruit or seed coat revealed the need for immediate washing and reduction of moisture to avoid decay. The type of seed and method of extraction affected oil yield (Figure 4) and (Table 6) (Gunstone, 1999; Marega et al., 2001).

Mechanical and hydraulic press of *C. megalocarpus* seed oil were found to be promising alternative seed oil extraction methods for rural areas (Pighinelli and Gambetta, 2012) because of the lower time taken, accessibility and the replacement of chemical solvent hexane (Table 6).

Higher seed oil yield of *C. megalocarpus* in other studies, about 49% (Munavu, 1983); 40%-45% (Aliyu et al., 2010); and 32% (Kafuku and Mbarawa, 2010) almost similar to *J. curcas* (Jumat and Rozaini, 2008) indicated the possible alternativeness of *C. megalocarpus* for biodiesel production (Wagutu et al., 2009). *C. megalocarpus* seed oil biodiesel showed higher calorific value comparable to petro-diesel (Okoro et al., 2011) (Table 8). The calorific value of biodiesel of *C. megalocarpus* of the present study (43.2 MJ kg^{-1}) was better than its biodiesel in Kenya (Wagutu et al., 2009). The flash point of the biodiesel of *C.megalocarpus* indicated its suitability for diesel engines (Table 8) (Osawa et al., 2014) with few saturated fatty acids in the ester mixture (Wu et al., 2013), which was affected by the method of seed oil extraction (Table 10) (Sakar et al., 2014). Similar to the present study, Wagutu et al. (2009) reported that the biodiesel of *C. megalocarpus* yielded methyl-9, 12-octadecadienoate about 86.6%, which is suitable for energy production. At the storage conditions, greater number of fatty acid was obtained at mechanical press in 25°C (Table 10), and further research on fatty acid composition is required between –20°C and 25°C storage.

It is known that Ethiopia's historical contribution to greenhouse gas emissions on a global scale was negligible (CRGE, 2011) but the high rate of indoor pollution requires production of biodiesel. *C. megalocarpus* is a potential alternative source of biodiesel for the rural Ethiopians cooking energy with reduced indoor pollution (Figure 5) which can also be

used as transport fuel (Osawa et al., 2014). Although the biodiesel could reduce end use emission from 38.90% to 39.42% of the firewood in a household level (Table 2), Gunvachai et al. (2007) stated that biodiesel on a lifecycle basis reduces net carbon-dioxide emissions by 78% when compared to petro diesel. *C. megalocarpus* that can produce biodiesel in addition to the desirable characteristics like 40 m height, 50% oil, 50% seed protein, seed cake poultry feed with low toxicity, and urban beautification (Noad and Birnie, 1989; Charles, 1990; Kibazohi and Sangwan, 2011) was not well utilized when compared with the common biodiesel crop, *J. curcas* in Ethiopia. Previous studies showed that *C.megalocarpus* is fast growing, producing seed after three years of age and grow in nutrient deficient dry areas (Aliyu et al., 2010; Kafuku et al., 2010) (Figure 7), and the present study found about 34 million hectare land area of Ethiopia could be suitable to grow (Figure 8), therefore, development oriented adaptation trial is highly required.

5 Conclusion and recommendation

Seed extraction, grinding and oil extraction method of seed is determined by the size, moisture and oil content of tree seeds. The biodiesel of *C. megalocarpus* can be an alternative source of rural household cooking energy in Ethiopia because it produced 50.2% (w/w) oil yield, up to 100% (w/w) biodiesel yield with 43.2 MJ kg^{-1} calorific value and 103°C flashpoint. If rural households use biodiesel instead of firewood and kerosene, they can reduce end use emission by 38.90% to 39.42%; and therefore, reduce indoor pollution. *C. megalocarpus* has oil, wood and seed cake feed value. Fatty acid composition of the biodiesel was affected by seed oil extraction methods. Since *C. megalocarpus* is a multipurpose tree species, it should be planted in suitable land areas of Ethiopia.

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