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Original Research Article

Investigation of Echinops Kebericho Mesfin Seed Oil as a Biodiesel Production Feedstock: Opportunities From the Wilderness

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Abstract

The major energy sources of the world depend on coal, natural gasses and petroleum which are exhaustible and environmentally unfriendly. Biodiesel is a mono alkyl organic compound of long chain of fatty acids made of oil from plant oils and animal fats that make use of a catalyst and an alcohol, which may be utilized in traditional diesel engines to function as an option for petro-diesel or blended with petro-diesel to diminish emissions. *Kebericho* seed oil which is endemic to Ethiopia was studied with the objective of investigating as a possible raw material for biodiesel production in this work. The *kebericho* seed that was extracted at 40 °C exploiting n-hexane as solvent yielded 26.7 %w/w oil. The Crude *kebericho* seed oil was transesterified at 60 °C for 90 minutes using oil/methanol ratio of 1:6 and 1% weight of KOH as a catalyst, to supply its resultant methyl ester compound. The resultant *Kebericho* oil methyl ester yield was found 92%. The fatty acid profile determination was carried out using gas chromatographic analysis and *Kebericho* oil methyl ester showed that it had been largely composed of palmitic, stearic, linoleic, oleic and linolenic esters that are comparable to the profile of sunflower, safflower and soybean oil. The fuel properties of *Kebericho* oil methyl ester were determined using the international standard for pure biodiesel using ASTM standard and each of the measured *Kebericho* oil methyl ester fuel properties were satisfied the ASTM D6751 biodiesel standards. Results from this study have clearly suggested the capability of *kebericho* seed oil as a biodiesel feedstock. Besides, as *kebericho* is thought to be invasive in Ethiopia, such conceivable outcomes of creating biodiesel from such species could be considered as one future management option with potential noteworthy economic returns and environmental advantages.

Key words: Invasive, Echinops kebericho Mesfin oil, transesterification, Purification, Biodiesel.

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1. Introduction

World markets for fossil oil and other liquid fuels have entered a time of dynamic change—in each supply and demand. Potential new supplies of oil from tight and shale resources have raised optimism for crucial new sources of worldwide liquids [1]. The longer term international economy is prone to consume ever a lot of energy, significantly with the rising energy demand of developing nations. Within the meanwhile, the large danger of global climate change connected with the use of fossil fuels makes supply this energy increasingly troublesome [2]. The substantial sources of energy needs are coal, natural gasses and oil, which are non-renewable and environmentally unfriendly. Insufficiency of the traditional fossil fuels, its over-reliance by countries, increasing emissions of burning created pollutants and their increasing expenses have created renewable energy sources a lot of engaging. For over a century, the use of vegetable oils, as an example, soybean, palm, sunflower, peanut and vegetable oil as fuel substitutes for fossil-based diesel has been around [3].

Biodiesel is an alternative fuel made up of vegetable oils or animal fats that can be used in traditional diesel engines to work as a substitute for petro-diesel or blended with petro-diesel to reduce emissions. In recent times, biodiesel has becoming more attractive substitute because it is derived from renewable resources, environmentally friendly, biodegradable and non-toxic in nature. It can moreover be made from any material that contains unsaturated fats, either associated with molecules or present as free unsaturated fats [4].

Echinops kebericho Mesfin (*kebericho*) has a place with the types of the genus Echinops, which is one of the genera assembled under the family Asteraceae. This genus is reported to represent more than 120 species, of which four (Echinops kebericho Mesfin, E. buhaitensis Mesfin, E. ellenbeckii O. Hoffm and E. longisetus A. Rich) are generally dispersed in the Ethiopian high lands. *kebericho* is so far known from a few of areas in Ethiopia. It is an erect lasting herb or bush up to 1.2 m high, commonly from a colossal root stock with verdant stems. The leaf lamina is curved and is detached into pieces that consistently end in spikes. The corolla is white or brilliant blue [5].The bases of *kebericho* are customarily utilized as a fumigant, for the most part after labor. It is guaranteed that the smoke is viable against typhus and fever. Individuals in the focal and south-western parts of Ethiopia utilize the smoke of *kebericho* to repulse snakes from their region [6]. Infusions of roots of *kebericho* are connected for the treatment of headache, looseness of the bowels, heart torment and different diseases [7]. *kebericho* is not reported as a biodiesel feedstock in this way.

kebericho is among the invasive species; threatening urban green spaces, rangelands, national parks, roadsides and agricultural lands [8]. The management need for controlling invasive plant species might be costly and need technical expertise. However, introducing options that can convert such species to an economical usable form can be overwhelming in a way of managing them and generating significant income besides to sustaining safe environment [9].

The main objective of the current study was to examine the employment of genus *kebericho* seed oil as a possible feedstock for biodiesel production. The fuel properties of the genus *Kebericho* oil methyl ester were determined and compared with biodiesel fuels from typical vegetable oils.

2. Materials and Methods

2.1. Materials

The seed of *kebericho* was collected from the local area of Mekelle and brought to the laboratory for this study. Analytical reagent methanol (99.8% purity) and sodium methoxide (95%) were purchased. Biodiesel D6584 kit (containing reference standard solution: triolein, diolein, monoolein, glycerol and the two internal standards: butanetriol, and tricaprin of >99% purity) was also purchased from Ethiopia. All the chemicals used were analytical reagent grade.

2.2. Methods and data analysis

2.2.1. Moisture content determination and oil extraction

The moisture content of the *kebericho* seeds was determined using an oven. The sample was weighed to the nearest 10 g in petri dishes and then dried at 105 °C. It was then cooled in desiccator over silica gel (0% relative humidity) and reweighted until the constant weight is maintained. The moisture content was determined as in equation 1:

$$M = \left(\frac{W1 - W2}{W1}\right) x\ 100\ \% \qquad (1)$$

Where M, W_1, W_2 are moisture content, initial mass and final mass respectively.

2.2.2. Oil extraction

The endemic *kebericho* seeds were collected from a neighboring area and dried. There after the *kebericho* seeds grinded using blender in order to expose large surface area of the cells containing oil for the extraction of the oil [10, 11]. The oil was leached for 8 hours using n-hexane as a solvent to seed powder with a quantitative ratio of 3:1 till pure hexane. Extraction mixture was cooled and filtered to remove the solid from the solvent. The solvent within the oil was removed employing rotary evaporator at 40 °C and used in the next batch. The oil obtained was weighed and therefore the oil yield was calculated by equation 2:

$$EKM \text{ oil content } = \frac{W_o}{Ws} x 100\ \% \qquad (2)$$

Where: W_o = weight (g) of oil extracted and

W_s = weight (g) of sample (dry base)

2.2.3. *kebericho* Seed oil analysis

The physical and chemical characterization of the oil was conducted first to see if pretreatment was necessary or not before transesterification. The quality properties of the oil were determined including kinematic viscosity, iodine value, density, saponification value, free fatty acid, acid value and higher heating value (HHV). The oil physical and chemical properties were analyzed using ASTM D6751 standards. All parameters were reportable as a mean values when triplicate experiments were run.

2.2.4. Transesterification

The crude EKMSO was heated at 105 °C to remove any moisture that hinders transesterification. The transesterification of the oil was completed in a 1 L two-necked round bottom reactor equipped with a thermometer under the oil bath, a hot plate with magnetic stirrer, and a reflux condenser. The reactor was initially loaded with 100 g of crude *kebericho* seed oil, which was preheated to the desired temperature before starting the reaction. The reaction was carried out at 60 °C for 1:30 h with 1 %wt of KOH and methanol-to-oil molar ratio of 6:1 [12]. In order to maintain the catalytic activity, a mixture of KOH and methanol was freshly prepared to avoid methanol losses and prevent moisture build-up. This was mixed until the complete dissolution of the catalyst. The solution was added into the reactor and stirred at 360 rpm. The reaction time began when the catalyst/methanol solution was added to the reactor. On completion of the reaction, the resulting product was cooled to room temperature with no agitation and transferred to a separatory funnel for glycerol and methyl ester separation. It was left for overnight to allow separation by gravity after which the content separated into two layers with the top mainly water and methanol and the bottom transesterified oil. After separation of the two stages, the upper stage was collected and the excess alcohol in it removed utilizing a flash evaporator operated at 90 °C. The resulting methyl ester acquired was purified by successive washing with warm deionized water to remove remaining catalyst, glycerol, methanol and soap. A little amount of tannic acid was utilized as a part of the second washing to neutralize remaining soaps and catalyst. At long last, the *kebericho* oil methyl ester was dried over anhydrous sodium sulfate to remove remaining water [13]. A filtration procedure took after to remove solid traces. This experiment was run in triplicate and mean value was reported.

2.3. Biodiesel yield

Biodiesel yield estimation was done after the separation and purification of the transesterified product. The biodiesel yield of the purified biodiesel was calculated according to equation 3.

$$\text{Yield} = W1/(W2)x\,100\% \qquad 3$$

Where; W_1= Weight of methyl ester produced (g)

W_2 = Weight of oil used in reaction (g)

2.4. Gas chromatography analysis

The fatty acid composition of the EKM oil biodiesel was investigated using gas chromatography. (DANI GC 1000) coupled with a flame ionization detector (FID) was used to analyze the fatty acid composition and ester content of *kebericho* oil biodiesel obtained from the transesterification reaction. The GC was calibrated by injecting standards at varying concentrations. The samples were injected (1µL) one by one in a DANI GC 1000, equipped with a capillary column of EC TM-5 (25 m x 0.53 mm x 1 µm). The GC oven was primarily kept at 50 °C for 2 min, and then heated at 4 °C /min up to 250 °C, where it was kept for 15 min, and a pressure of 1.25 Bar was applied. Nitrogen was the carrier gas used at a flow rate of 1 ml/min.

2.5. Biodiesel property determination

Fuel properties of *kebericho* methyl ester, such as density (ASTM D4052), kinematic viscosity (ASTM D445), flash point (ASTM D93), cloud point (ASTM D2500), acid value (EN 14104and HHV (ASTM D240), were measured according to relevant biodiesel test methods. The cetane number of *kebericho* methyl ester was evaluated using empirical formula reported in the literature [14] as given below and from a published work [15] to enhance the use of the formula:

$$\text{CN} = \text{XME (wt.\%)} \times \text{CNME} \qquad 4$$

Where CN, is the cetane number of the biodiesel, XME is the weight percentage of each methyl ester and CNME is the cetane number of individual methyl ester. All tests were run in triplicate and mean values were reported.

3. Results and Discussion

3.1. Percentage oil content of kebericho seed oil

The moisture content of the *kebericho* seed was found 4.4%w/w. Following the moisture content determination the oil content of the collected seeds was determined and found approximately 26.7 %w/w (in weight basis) using hexane as extraction solvent.

3.2. Physicochemical properties of *kebericho* seed oil

The quality of *kebericho* seed oil was expressed in terms of selected physicochemical properties as shown in Table 1. The acid value and the saponification value of the oil were 0.92 and 188.48 mg KOH/g, respectively. With acid value of 0.92 mg KOH/g corresponding to 0.46% free fatty acid (FFA) content, transesterification of the oil was conducted directly (using a single-step reaction process) [16]. Moreover, it has been reported that <0.5% FFA content is required for successful transesterification to avoid soap formation resulting from high free fatty acid [16, 17]. The kinematic viscosity of crude EKMSO was 33.13mm^2/s (Table 1), which was similar to that reported for safflower and soybean oil [18]. The density and HHV of the oil were determined to be 901.1 kg/m3and 38.46 MJ/kg, respectively. These results are well within the range reported for conventional vegetable oils [18].

The fatty ester profile of *kebericho* oil methyl ester, as determined by gas chromatography is provided in Table 2. It was found that EKMOME composed of six fatty acids: palmitic, palmitoleic, stearic, oleic, linoleic and linolenic acids. Of the six fatty acids, linoleic acid is the most prevalent with the value of 60.31%.

Table 1. Physicochemical properties of *kebericho* seed oil

Parameter	*kebericho oil*
Iodine value (g I2/100g)	112.06
Density at 15 °C (kg/m3)	901.1
Kinematic viscosity at 40 °C (mm2/s)	33.13
Saponification value (mg KOH/g)	188.48
Acid value (mg KOH/g)	0.92
Free fatty acid (%)	0.46
Caloric value (MJ/kg)	38.46

The total saturated and unsaturated fatty acid contents of the seed oil were 29.20 and 70.80% respectively. Palmitic acid (17.44%) was the predominant saturated fatty acid. For comparison purpose, the fatty acid compositions of palm, safflower, sunflower and jatropha oils are listed in Table 2. As shown in Table 2, the fatty acid profile of *kebericho* oil methyl ester (especially in terms of total unsaturation) was similar to that of sunflower, jatropha and safflower oils but not palm oil. *kebericho* oil methyl ester has a fatty acid profile which resembles those of some conventional oils (soybean, rapeseed, sunflower, cotton, corn) with oleic and linoleic acids being the major acids [19] which signifies its probable use as biodiesel production feedstock in terms of its chemical composition and oil properties.

Table 2. Fatty acid compositions (wt %) of vegetable oils and *kebericho* oil methyl ester

Fatty acid	Class	Sunflower[20]	Safflower[20]	Jatropha[21]	Palm[20]	*kebericho* oil methyl ester
Caprylic	C8:0	0.0	0.0	0.0	0.1	0.0
Capric	C10:0	0.0	0.0	0.0	0.1	0.0
Lauric	C12:0	0.0	0.0	0.0	0.9	0.0
Myristic	C14:0	0.1	0.1	0.0	1.3	0.0
Palmitic	C16:0	6.0	6.6	18.22	43.9	17.44
Palmitoleic	C16:1	0.0	0.0	0.0	0.0	0.04
Stearic	C18:0	5.9	3.3	5.14	4.9	11.76
Oleic	C18:1	16.0	14.4	28.46	39.0	9.97
Linoleic	C18:2	71.4	75.5	48.18	9.5	59.31
Linolenic	C18:3	0.6	0.1	0.0	0.3	1.48
Total saturated		12.00	10.00	23.36	51.20	29.20
Total unsaturated		88.00	90.00	76.64	48.80	70.80

3.4. Biodiesel yield

Biodiesel yield estimation was done after the separation and purification of the transesterified product. The 92 % yield of *kebericho* seed oil synthesized was calculated according to Equation 2. Naturally occurring vegetable oils and animal fats are known to contain tocopherols,phospholipids, sterylglucosides, chlorophyll, fat soluble vitamins, and hydrocarbons. Some of these impurities are insoluble and can be removed by filtration while others are soluble. The soluble part can only be removed by different refining processes. It has been reported that the reduced yields in biodiesel production with raw oils could be as a result of the presence of solids and extraneous material in the oils [13]. The negative impact impurities present in oil have on ester yield has been stressed

[22]. Furthermore, under the same reaction conditions, 67 to 84% ester conversion can be obtained using crude vegetable oils, compared with 94 to 97% when using refined oils [23]. Previous studies on the transesterification of crude oils of tobacco seed [19], karanja [24], sesame [25] and rice bran [26] reported 84, 86, 74 and 83.31% ester yield, respectively.

3.5. Biodiesel properties of EKMOME

The biodiesel produced from *kebericho* oil was analyzed for its fuel properties. Table 3 shows the summary of the properties of the biodiesel of *kebericho* oil. The properties of *kebericho* oil biodiesel were within the mentioned biodiesel standards, ASTM D6751 and EN 14214 except for the Carbon residue

Table 3. Fuel properties of *kebericho* oil biodiesel

Property	Units	Test Methods	Limits		EKMOME
			ASTM D6751	EN 14214	
Density (15^{0}C)	kg/m³	D1298	--------	860–900	886
Kinematic viscosity(40ºC)	mm ²/s	D445	1.9 -6.0	3.5-5	3.88
Gross calorific value	MJ/kg	D240	--------	-------	39.27
Cloud point	°C	D97	Report	-------	1
Ash content	W%	D874	0.02 max	0.02 max	0.01
acid value	mg KOH/g	D664	0.5 max	0.50 max	0.18
Carbon residue	% mass	D189	0.05 max	0.3max	0.32
flash point	°C	D93	93.0 min	120 min	122
Copper corrosion	Max.	D130	No. 3 max	No. 1 max	1a
Distillation, 90% recovery	°C	D86	360 °C max	-----	339
Cetane number		-	47 min	51 min	52.55*

*: Empirically determined

4. Conclusions

Aiming the *kebericho* seed oil as a potential alternative feedstock for biodiesel production, around 26.7 %w/w was extracted and characterized. *kebericho* seed oil was transesterified using methanol in the presence of KOH to produce *kebericho* oil methyl ester. The prepared *kebericho* seed oil biodiesel gave promising results as alternative diesel fuel with fuel properties in good agreement within limit set by international biodiesel standards (EN 14214 and ASTM D6751). Fuel properties and fatty acid composition of *kebericho* oil biodiesel were found to be synonymous to those of soybean, sunflower and safflower biodiesel which have been well established and widely published. It is worth mentioning that *kebericho* oil methyl ester has a remarkably low kinematic viscosity compared to most biodiesel. This present study has justified the use of *kebericho* seed oil as a potential raw material for biodiesel production. The use of such invasive species for biodiesel not only solves their management challenge but also add to the economic and environmental benefits that can derive from such resources in the wilderness.

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