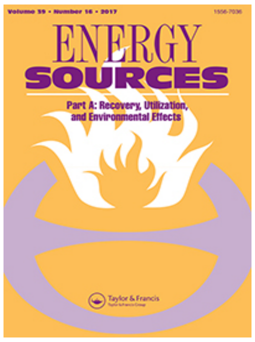

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Solanum nigrum L. as a novel energy resource for biodiesel production through transesterification process using an open-system reactor

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ABSTRACT

Biodiesel is one of the paramount biofuels and alternates for geologically produced petroleum fuel. The lipid sources in dissipate material are very much valuable in two ways: one is for the remediation of dissipate and the other is to obtain a high percentage of biofuel. Hence, in the present study *Solanum nigrum* L. seed – a widespread weed found in agricultural fields – was selected as a source to produce biodiesel via the transesterification process with the help of an alkali catalyst. The highest conversion of *Solanum nigrum* L. seed oil (as triglyceride) to biodiesel was achieved as 99.6 wt% with 35 min reaction time at 65°C, 9:1 molar ratio of methanol to oil, and 1 wt% of potassium hydroxide (KOH) catalyst. At the optimized condition, the conversion of triglyceride to biodiesel was confirmed by ^{1}H NMR and the fuel properties of biodiesel were analyzed. The fuel properties were originated to be observed within the limit of ASTM D6751 standard.

KEYWORDS
Biofuel; novel energy source; transesterification; biodiesel; *Solanum nigrum* L; alkali catalytic process

Introduction

The modern crisis of contamination of the environment caused by the flaming of fossil fuels as well as their declining reserves is motivating research into the development of renewable and sustainable biofuels (Razif Harun, Jason, and Danquah 2011). Biodiesel fuel, which consists of the straightforward alkyl esters of fatty acids, preferentially alkyl esters, has obtained a growing interest as an option to diesel fuels made from renewable energy sources. Biodiesel has two main compensations, the alleviation of carbon dioxide and as a replacement for petroleum (Chisti 2008). In addition, to meet the environmental criteria and for engine performance, biodiesels have to compete economically with diesel fuels in order to stay alive in the market. One approach of reducing biodiesel production costs is to use the less-expensive energy sources as feedstocks (Ramachandran et al. 2011; Suganya, Kasirajan, and Renganathan. 2014).

The use of suitable for eating vegetable oils and animal fats for fuel production received huge concern for the reason that they compete with food materials (Kalam et al. 2008). The claims for vegetable oils for food have amplified enormously in current existence. It was impracticable to provide a reason for the use of vegetable oils for biodiesel fuel purposes such as biodiesel production. Additionally, vegetable oils are more expensive to use as fuel energy (Demirbas A.H., 2009). The utilization of nonedible place in the ground oil sources are keeping opposition with food edible oil for biodiesel production feed sources.

In the management of wastes, exploitation of waste matter is very helpful for the community (Gray, Zhao, and Emptage. 2006). Because it is very economical, contains a rich amount of lipids (in

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case of agricultural wastes), and is easy to gain, the remediation of waste matter is an alternate solution with by-products such as biofuel (Casida 2010). Consequently, the involvement of nonedible oil from *Solanum nigrum* L. will be one potential resource for biodiesel fuel production. The oil from the tropical plant *Solanum nigrum* L. is nonedible, which has an incredible prospective for biodiesel fuel production. Additionally, it grows naturally in wastelands, thereby providing a more attractive resource for biodiesel production.

Solanum nigrum L, also called "black morelle", is a yearly herbaceous plant of 10–60 cm height, with a green, soft, and partially mountain-climbing stem. The conflicting leaves, with whole limb, oval and diamond-shaped, are somewhat cogged. It is a moderately common species in wet woods, in close proximity to rivers and old walls. It grows nearly everywhere in Africa and America. In India, *S. nigrum* L, along with other herbal medicines, has a hepato-protective effect in cirrhotic patients. This protective outcome can be attributed to the diuretic, antioxidative, anti-inflammatory, and immune-modulating properties of the constituent herbs (Fallah Husein et al., 2005). It also protects against hepatitis B virus disease B (Galitskii et al., 1997; De Silva et al., 2003; Kalab, 1997). *S. nigrum* L is particularly known for its toxicity because it contains a neurotoxic glycol-alkaloid, solanine (Abbas et al., 1998). The extracts of its fruits have neuro-pharmacological and antitumor properties and they can be used as a cancer chemopreventive and antioxidant matter (Perez et al., 1998; Son et al., 2003).

A review of the literature showed that no effort has been established so far on the production of biodiesel using the new *S. nigrum* L. The main objective of the current study is to extract lipid present in the renewable source of *S. nigrum* L by the Soxhlet extraction process for the production of biodiesel. Then the potassium hydroxide (KOH) catalyst was used to catalyze the transesterification reaction for the invention of methyl ester from the extracted oil of *S. nigrum* L. This will increase the utilization of waste oil renewable resource, reduce environmental pollution, and further reduce the biodiesel production costs by using less-expensive waste source.

Materials and methods

Materials

The *Solanum nigrum* L seeds were collected in and around Jimma town in Ethiopia. KOH used as alkali catalysts for the straight transesterification reaction was purchased from Sisco Research Laboratory Ltd, Mumbai, India. The chloroform analytical grade with 99.9% purity was purchased from Sisco Research Laboratory Ltd, Mumbai, India; hexane analytical grade with 99% purity and methanol analytical grade with 99.9% purity were purchased from Merck India Ltd., Mumbai, India; these solvents were used for extraction purposes.

Pretreatment followed by the extraction and characterization of oil

Solanum nigrum L seed was initially weighed, and then moisture was removed in a hot oven at 45°C until it reached equilibrium state. Around 3.6 wt% of moisture was removed from the seed (moisture content of the fresh *Solanum nigrum* L seed was analyzed by the gravimetric technique). The moisture-less seed was crushed and separated based on the size of the granular particle by sieving as per the ASTM standard. Later, 0.25 mm of the particles were taken for the superheated solvent extraction process and it was carried out with the missed solvent system of hexane, chloroform, and methanol at the ratio of 3:2:1, respectively (Ramachandran et al., 2014).

Properties such as average molecular weight, density, iodine value, acid value, saponification value, and FFA content of the extracted *Solanum nigrum* L oil were analyzed using standard procedures (AOCS, 1998; Vicente., Martinez, and Aracil. 2004). The *Solanum nigrum* L oil (reactant) samples were taken and fatty acid composition analysis was carried out by gas chromatograph in Chennai, Tamilnadu (Sam et al. 2008).

Transesterification process and biodiesel characterization

In this research study, the *Solanum nigrum* L seed oil was used as an energy source main reactant. The molar ratio of methanol to *Solanum nigrum* L seed oil required was estimated by treating 3 moles of free fatty acid as 1 mol of triglyceride. The transesterification reaction procedure was performed in a three-neck flat-bottom flask as an open system reactor, equipped with a magnetic stirrer and a temperature indicator. The *Solanum nigrum* L nonedible seed oil was charged into the reactor. When the required transesterification reaction temperature was reached, methanol and KOH mixture was added into the reactor. Afterward, the transesterification reaction was stopped after reaching the required time. Then, the reacted mixture was allowed to settle down overnight. The top layer of biodiesel–methanol mixtures was then separated from crude glycerol mixtures and allowed to distill excess of methanol.

The ^{1}H NMR spectra of biodiesel were recorded on a Bruker, Advance III instrument, 500 MHz NMR, Switzerland. The conversion of biodiesel estimated by the assimilation values of the protons of the methyl ester moiety was deducted at around 3.6–3.7 ppm and for the carbonyl methylene groups it was deducted at about 2.3 ppm in all fatty acid compounds (Gelbard et al. 1995; Knothe G and Kenar JA, 2004). The fuel properties of the biodiesel were strong-minded by the ASTM test methods and weighed against the ASTM D6751 standards.

Result and discussion

Characterization of Solanum nigrum *L. seed oil*

One gram of *Solanum nigrum* L. seed oil was taken and chemical analysis was carried out by gas chromatography, which consists of the CHEMIT GC 8610 flame ionization detector in the column BPX-70. Nitrogen and hydrogen gases were used as the carrier gas and O_2 was used for ignition purposes. The data were composed with Winchrom software. The composition of the fatty acids was found to be as follows: palmitic acid (C16:0) 11.05%, stearic acid (C18:0) 4.86%, oleic acid (C18:1n-9cis) 15.32%, linoleic acid (C18:2n-6cis) 67.48%, α-linolenic acid (C18:3n-3cis) 0.91, stearidonic acid (C18:4n-3) 0.32, and the rest are tri-di-mono glycerides and traces of impurities. The saturated, mono-unsaturated, poly-unsaturated, and total unsaturated fatty acids were found as 15.91, 15.32, 68.71, and 84.03, respectively, and the other properties are listed in Table 1. Consequently, *Solanum nigrum* L seed oil as a nonedible source is highly suitable for biodiesel production. The direct transesterification process was selected for this resource, because the free fatty acids content was found to be less than 1%. Hence, the transesterification process without any further pretreatment of *Solanum nigrum* L seed oil was chosen for biodiesel production.

Reaction studies

Temperature effects on transesterification with respect to time

Initially, triglyceride needs to stimulate its individual carbonyl functions to initiate the transesterification reaction (Al-Widyan MI and Al-Shyoukh AO, 2002). The lengthy alkyl manacles in a triglyceride molecule can get in the way with the activation of its carboxylic assembly. The activation

Table 1. Properties of *Solanum nigrum* L seed oil.

S. No.	Properties	Values
1.	Molecular weight (average)	872.44 g/mole
2.	Viscosity	32.65 mPa.s
3.	Acid value	1.6 mg KOH/g
4.	Saponification value	186.2
5.	Iodine value	103.15
6.	Free fatty acids	0.8%

of triglyceride is extremely complicated. To support the methanol nucleophilic assault on the triglyceride, a moderately elevated reaction temperature is considered necessary to make this carbonyl group active. Therefore, the experimentations were conducted using KOH as a base catalyst at 45, 55, and 65°C with respect to various time intervals. The conversion of triglycerides to biodiesel is shown in Figure 1a. From the graphical representation, it can be observed that the conversion of Solanum *nigrum* L seed oil to biodiesel increased with increase in the transesterification reaction temperature. The equilibrium conversion of *Solanum nigrum* L seed oil was found to be reached by 30 min. The highest conversion of triglyceride was obtained as 90.2 wt% after reaching 40 min reaction time at 65°C.

Catalyst effects on transesterification with respect to time

In most cases, from the literature, it was observed that the concentration of alkali catalyst used for transesterification is less than or equal to 1wt% for the successful conversion of lipids to methyl ester depending on the nature of oil used (Felizardo et al. 2006; Hanh et al. 2007; Tomasevic AV and Siler-Marinkovic SS, 2003). The effect of KOH concentration was considered, with various concentrations series from 0.5 to 1.5 wt% to *Solanum nigrum* L seed oil. The additional parameters, such as 65°C of reaction temperature, 500 rpm of mixing intensity, and methanol to biomass ratio of 12:1, were maintained with various reaction times. The conversion of *Solanum nigrum* L seed oil to methyl esters was found to increase with an increase in the KOH catalyst concentration varying from 0.5 to 1 wt%. The highest conversion of 94.25% was achieved with 1 wt% of KOH concentration at 35 min. On further increase in the catalyst concentration above 1%, the conversion was found to decrease (Figure 1b). The accumulation of a surplus quantity of catalyst results in the creation of soap, which decreases the conversion by the generous expansion to emulsify glycerol and biodiesel phase. Hence, 1 wt% of KOH catalyst concentration was found to be an optimum point for the direct transesterification of *Solanum nigrum* L seed oil in an open system reactor.

Methanol-oil molar ratio on transesterification with respect to time

Methanol to oil molar ratio is one of the significant variables controlling the conversion of *Solanum nigrum* L seed oil into methyl esters. Although the stoichiometric mole ratio of alcohol to triglyceride for transesterification is 3:1, definitely higher molar ratios than the stoichiometric condition are required to enhance the biodiesel conversion (Noureddini, Harkey, and Medikonduru 1998). The methanol to oil ratio effect was studied in the range of 6:1, 9:1, and 12:1. Figure 1c shows the effect of methanol to oil molar ratio in the conversion of nonedible seed oil of Solanum *nigrum* L to biodiesel. It was observed that the conversion of the process enhances with an enhancement in the molar ratio. The optimum conversion of 98% was obtained at a methanol to oil ratio of 9:1 at a constant reaction temperature of 65°C and a reaction time of 35 min with 1 wt% of the KOH catalyst. With auxiliary increase in the molar ratio of methanol, the conversion decreases due to the mass transfer limitation.

Mixing intensity effects on transesterification

The effect of stirring on alkali (KOH)-catalyzed transesterification reaction was carried out at 65°C using a 9:1 molar ratio of methanol to oil with 1 wt% of potassium hydroxide catalyst. When a homogeneous catalyst is used at a moderate temperature of 65°C for transesterification, the *Solanum nigrum* L seed oil and methanol reaction mixture exhibits two phases. The continuation of two phases will reduce the reaction rate due to the strong mass transfer limitations (Aldo et al., 2010). It was observed that at the lower mixing intensity of 300 rpm, the reaction continued gradually during the commencement of the reaction, which provides a small conversion of *Solanum nigrum* L seed oil to methyl ester. The conversion of *Solanum nigrum* L seed oil was found to improve with an increase in the mixing rate. The highest conversion was achieved as 99.6% at 400 rpm and 35 min of reaction

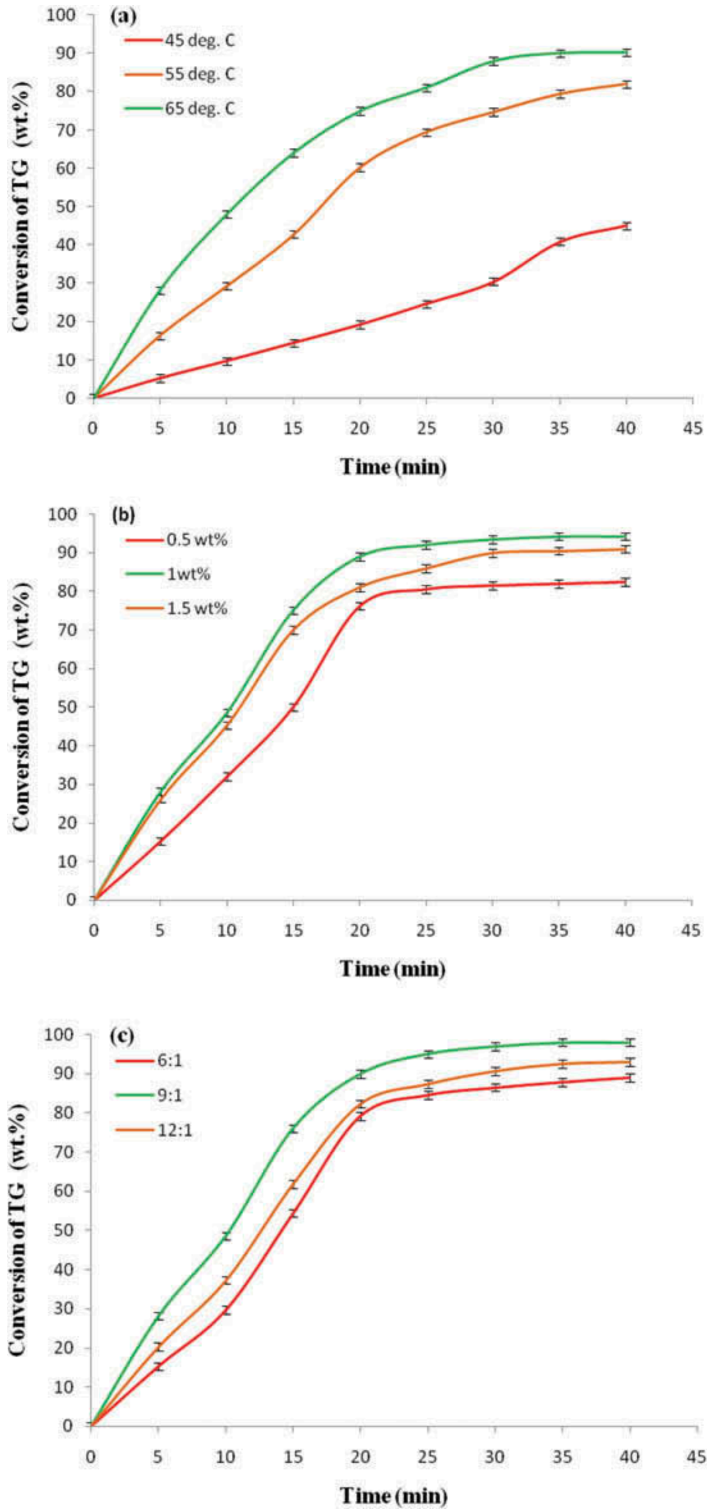

Figure 1. Reaction studies: **(a)** temperature effects on transesterification with respect to time, with 1.5 wt% of catalyst, 500 rpm of mixing intensity,and 1:12 molar ratio of oil-methanol; **(b)** catalyst effects on transesterification with respect to time at 65°C, 500 rpm of mixing intensity, and 1:12 molar ratio of oil-methanol; **(c)** methanol-oil molar ratio on transesterification with respect to time at 65°C, 500 rpm of mixing intensity, and 1 wt% of catalyst.

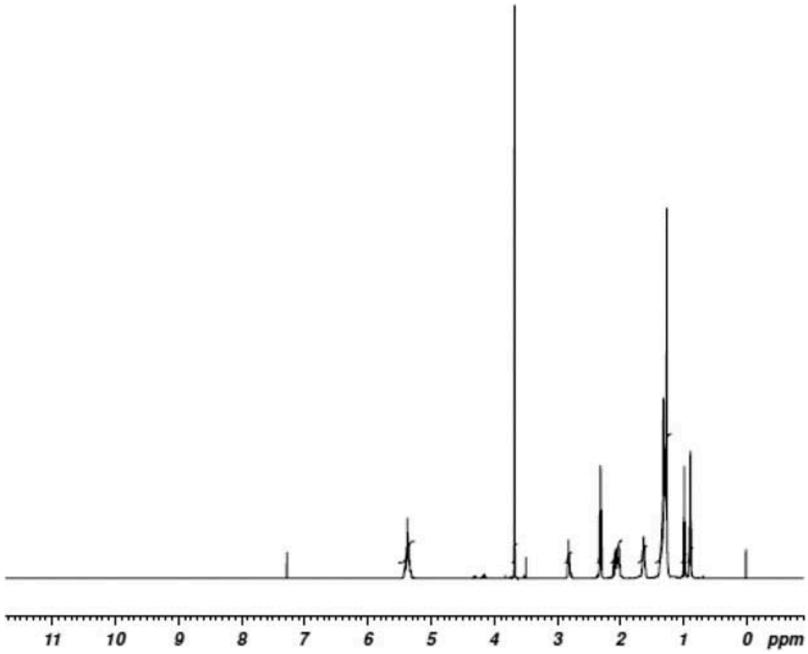

Figure 2. [1]H NMR spectra for the confirmation of *Solanum nigrum* L biodiesel.

time; it was confirmed by [1]H NMR spectra shown in Figure 2. Further enhancement of the mixing rate to 500 rpm decreased the conversion; this clearly indicates that mass transfer limitations (diffusion controlling steps take place at a higher mixing rate, which means the interaction between the reactants was restricted) play a major role during the transesterification reaction at moderate temperature. With the intention of overcoming this problem, the reaction was examined at a higher stirring rate of 400 rpm.

Fuel properties of Solanum nigrum *L biodiesel*

The fuel properties of biodiesel obtained from a nonedible source of *Solanum nigrum L* were determined using standard techniques and are shown in Table 2, and also judged against the properties of *Solanum nigrum L* biodiesel with conventional diesel and ASTM D6751. However, the properties of methyl ester such as kinematic viscosity, density, flash point, cetane number, cloud point, pour point, cold filter plugging point, water content, sulfur content, and ash content are similar to those of conventional diesel and met the limits of the ASTM D6751 standard.

Table 2. Fuel properties of *Solanum nigrum* L biodiesel with ASTM D 6751 and ASTM D 975.

Fuel Properties	Solanum nigrum L Biodiesel	Petroleum Diesel ASTM D 975	Biodiesel ASTM D 6751
Density (kg/m^3)	870	850	820–900
Kinematic viscosity @ 40°C (mm^2/s)	3.8	2.6	1.9–6
Cetane number	51	48	47 min
Flash Point (°C)	140	68	130 min
Water content (wt%)	0.01	0.02	0.05 max
Ash content (wt%)	0.01	0.01	0.02
Sulfur content (mg/kg)	Nil	50 max	15 max
Methanol (wt%)	0.02	-	0.2 max
Acid value (mgKOH/g)	0.15	-	0.5 max
Cu corrosion (3Hr/50°C)	1a	1	3 max

Conclusion

This research study highly structured the utilization of the nonedible source of *Solanum nigrum* L seed as a potential feedstock to produce high-quality biodiesel fuel. The direct transesterification of *Solanum nigrum* L oil was discussed and shown to result in an increased conversion of 99.6%. An optimization study was carried out with the parameters to obtain a higher conversion; this was confirmed by the ^{1}H NMR analysis. *Solanum nigrum* L oil has potential applications in biodiesel production. The production of *Solanum nigrum* L biodiesel could be a supplementary value to an unutilized agricultural product. *Solanum nigrum* L has excellent opportunities for agriculturists in addition to industrialists.

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