Fuel Processing Technology 133 (2015) 173–182

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Synthesis and characterization of biodiesel from Aamla oil: A promoting non-edible oil source for bioenergy industry

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ARTICLE INFO

Article history:
Received 9 November 2014
Received in revised form 12 January 2015
Accepted 13 January 2015
Available online 16 February 2015

Keywords:
Aamla oil
Biodiesel
Blends
Characterization
Physico-chemical properties

ABSTRACT

In the present research work, non-edible oil source Aamla plant was systematically identified for biodiesel production. The extracted oil percentage was achieved by up to 37.22% of the total dry seed weight. The free fatty acid content of crude oil was reduced from 4.12 mg KOH/g to 0.13 mg KOH/g, using esterification before the synthesis of biodiesel. The highest conversion yields of biodiesel were achieved at 88.77 & 90.31%, respectively using solid base catalyst oxides. The protocol for experiments was adjusted as follows: temperature (60 °C); different catalysts with various concentrations, time of reaction (2 h), stirring velocity (600 rpm) and 1:6 oil molar ratios. Qualitatively, the prepared biodiesel was characterized by GC chromatography, ^{13}C & ^{1}H NMR, FT-IR and AAS spectroscopy. In terms of fuel properties, the kinematic viscosity, density, Cloud Point, Pour Point, Cold Filter Plugging Point, acid number, Flash Point and cetane number of prepared biodiesel, its 4 blends i.e. B5, B10, B15 & B20 and petro-diesel sample were tested and compared with ASTM D6751 and EN 14214 standards.

1. Introduction

Due to billions of tons of carbon emissions into the atmosphere, global temperature rises, threats of climatic changes and the great obstacles to further development of conventional energy sources. Scientists and policymakers have focused on a range of friendly renewable energy technologies to replace the burden of imported fossil oil. In this context, biodiesel got a significant attraction on the future scenario of energy. Until recently, biodiesel has been produced from edible oils such as sunflower, soybean, and palm. However, the use of edible oils created many problems, particularly, the insecurity of food industry in most of the under-developed countries thus forcing the scientific communities worldwide to focus on their research efforts to make sure that the utilization of non-edible sources for the production of biodiesel is not competing with the edible food crops or vegetable oil.

The term biodiesel is defined as “a mono-alkyl ester consisting long chain of carbon derived from various plants and animals fats”. In this context, for the production of biodiesel, different types of edible and non-edible oil resources have been excised to obtain an economic yield of biodiesel, including soybean oil, used oil from frying industry, rapeseed oil, neem plant oil, wild safflower oil, castor plant oil and palm oil [1–3].

The concept of biofuel (biodiesel), as an alternative petro-fuel, has been gaining wide importance throughout the world for its quality, low emission, biodegradability, portability and sustainability [4]. Mankind is too much dependent on fossil fuels that it is beyond imagination to think about development and prosperity without them. Petro-fuels are present in a limited quantity and it takes millions of years for their synthesis [5]. No doubt, various renewable and sustainable resources of energy such as solar, wind, geothermal and hydropower have already been exploited worldwide but currently the role of biofuel, especially, in the transport sector, is considered to be of utmost importance. Also, the choices of potential raw materials for biodiesel production, their availability and cost are important aspects that need to be investigated thoroughly.

Among the available resources, one of the most potential raw materials available for biodiesel production is Aamla oil. Aamla (*Phyllanthus emblica* L.) is a perennial plant. It grows up to 12–22 m. Plant wood is red, hard bark and smooth. The leaves are pinnate but usually floriferous towards the base, falling as a unit. Foliage leaves are 85–140 per shoot, leaf blades linear to oblong, 0.6–1.5 × 0.1–0.4 cm. Lateral pairs of the nerves are 4–9 pairs, light green above to somewhat grayish below. Stipules of the cataphylls triangular ovate, 1.6 mm. Flower; the male flower pedicel is slender, 1–2.1 mm, sepals are 6 in numbers, oblong to oblanceolate, 1.4–2.1 × 0.4–0.7 mm, stamens 3, the filaments completely connate into a short terete column, anthers sessile. Female

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http://dx.doi.org/10.1016/j.fuproc.2015.01.013
0378-3820/

flower is sub-sessile; sepals thicker than those of the male and somewhat denticulate, otherwise similar; ovary ovoid, 3 celled up to 1 mm in diameter. The fruit is sub-globose 2.6 cm in diameter and the seeds are somewhat unequally trigonous as shown in Fig. 1.

It is a perennial deciduous tree. It commonly grows in well dried places. Irrigated and in open environment. It flourishes in the altitudinal range from 610 to 1370 m. The Aamla plant tolerates an annual precipitation up to 1018–1312 mm and temperature of 24–29 °C, respectively. It is distributed in many parts of China. The main regions include: Fujian, Guangdong, Hainan, Jiangxi and Sichuan provinces. It has also been cultivated in the subtropical countries i.e. Malaysia, Indonesia and Sri Lanka. In Pakistan, India, Bhutan, Nepal and Myanmar, it is distributed near the Himalaya foot [6].

Oil yielding plant species have been one of the most important sources of raw material for biofuel [7]. It is renewable, sustainable and comparative to petro-diesel oil, reduces overall the global warming to about 78%. In addition, excellent lubricity, outstanding biodegradability, high combustion efficiency and low viscosity are its other advantages [8–11].

It has been noticed from the literature survey that yet, systematically, quantitatively and qualitatively no work has been done on Aamla oil. Attempts have been made to describe the optimized method for quantitative production and to qualitatively determine the Aamla methyl esters for commercialization. The qualitative, quantitative study on available biomass resources for biodiesel production has been the subject of different advanced publications.

In this research work, the major physico-chemical properties such as kinematics viscosity, density, Cloud Point, Pour Point, cold filter plug point, Flash Point, sulfur content, cetane number, acid number, calcium, magnesium, sodium and potassium have been studied quantitatively. Various analytical techniques such as GC, NMR, AAS and FT-IR spectroscopy have been used for their authentication.

2. Materials

The Aamla plant mature seeds were collected through several visits from different parts of the country. The Aamla collected seeds after field collection were washed with warm distilled water to remove the dust and impurities. Later, the seeds were dried in an oven at 50 °C till their constant weight. The oil was extracted by electric oil expeller (German, KEK P0015-10127) and subsequently organic solvent extraction (soxhlet apparatus) to know the accurate oil contents [12]. The chemical reagents (i.e. methanol, chloroform, petroleum ether, *n*-hexane, phenolphthalein, isopropyl alcohol, sulphuric acid, anhydrous sodium sulfate, oxalic acid, methyl heptadecanoate, tetramethylsilane, lactic acid, nitrogen, potassium bromide, potassium hydroxide, sodium hydroxide, magnesium oxide, calcium oxide, lithium oxide, zinc oxide and magnetic oxide Fe–Ca) used in this experiments were purchased from Merck (Germany), Werner & Mertz (Germany), Abbott Laboratories (Pakistan) and Brookes (Pakistan) and are of analytical grade and used as such without any purification.

Fig. 1. Aamla plant dry seed sample.

3. Experimental section

3.1. Oil extraction

The dried seeds of Aamla (10 g) were crushed into thin powder through mortar and pestle. The thin powder was subjected to soxhlet apparatus fitted with 250 mL 3 necked round bottom flask and a reflux condenser. For accurate extraction, petroleum ether was used as a solvent. After extraction, the solvent was removed at 55 °C under a moderate vacuum using rotary evaporator. The percentage of extracted oil was determined using expression 1 [13].

$$\text{Percentage of the extrected oil;} \quad W4 = \frac{(W3-W1)}{W2} \times 100 \qquad (1)$$

where,

W_1	weight of empty flask
W_2	weight of powder sample
W_3	weight of flask and oil extracted.

3.2. Esterification reaction

Before the synthesis of biodiesel, the high free fatty acid content in Aamla filtered crude oil was esterified. The main objective of acid catalyzed esterification was to minimize the acid value of oil. The extracted oil acid value was analyzed using 1% (w/w) hydrochloric acid (H_2SO_4), which served as an acid catalyst [10].

3.3. Transesterification reaction

The process of transesterification reaction was carried out in 1/2 l 3 necked round bottom flask equipped with sampling outlet, reflux condenser, thermometer and magnetic stirrer. Approximately, 250 ml Aamla esterified filtered oil was heated. The temperature was maintained up to 120 °C for 1 h. The moisture and degraded mono-, diglyceride were removed from the acylglycerol, because of the reaction of these sodium and potassium oxides, which produce soap. The transesterification reaction of Aamla esterified oil was carried out at 1:6 molar ratio of oil/methanol, respectively using the following concentration 0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0, 2.25, 2.50, 2.75 and 3.0% (w/w) of sodium hydroxide (NaOH), potassium hydroxide (KOH), magnesium oxide (MgO), calcium oxide (CaO), lithium oxide (La_2O_3), zinc oxide (ZnO) and magnetic oxide (Fe–Ca) for protocol optimization. The temperature (60 °C), reaction time (2 h) and stirring velocity (600 rpm) were kept constant for the reactions. The resultant product after complete reaction was allowed to cool down at room temperature. The upper phase contained thin spot of soap and the middle part biodiesel, while the base phase contained gelatinous mass of glycerin and the mixture was separated by simple decantation. The main dogma of biodiesel preparation is presented in (schematic diagram) Fig. 2.

At the end, the mixture was separated into two layers, the upper layer contains Aamla crude biodiesel having an excess amount of methanol. The crude biodiesel was purified by residual methanol distilling at 65 °C for 60 min by a moderate rotary evaporator. The remaining catalyst together with other inorganic impurities formed soap and some catalyst was removed by consecutive washing steps with distilled