Energy 89 (2015) 887–895

Contents lists available at ScienceDirect

Energy

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

Assessing the experimental investigation of milk thistle oil for biodiesel production using base catalyzed transesterification

Kifayat Ullah [a,*], Mushtaq Ahmad [b], Sofia [b], Fengxian Qiu [c]

[a] Department of Biosciences, COMSATS Institute of Information Technology, Park Road, Chack Sahzad, Islamabad, Pakistan
[b] Biofuel & Biodiversity Lab., Department of Plant Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan
[c] School of Chemistry and Chemical Engineering, Jiangsu University, 212013 Zhenjiang, China

ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form
15 April 2015
Accepted 10 June 2015
Available online 17 July 2015

Keywords:
Milk thistle plant
Non edible oil
Two step process
MTOB
Chromatography
Spectroscopy

ABSTRACT

In the present research work, non edible oil source milk thistle (*Silybum marianum* (L.) Gaert) plant was investigated for biodiesel production. The extracted crude oil was 26.14% of the total seed dry weight. The free fatty acid content of oil was reduced from 0.56 mg KOH/g to 0.06 mg KOH/g by esterification before the synthesis of biodiesel. The highest conversion percentage of biodiesel was achieved 89.51% and 87.42% using solid base catalyst sodium hydroxide (0.75%) and potassium hydroxide (1.0%), respectively. The protocol for experiment was adjusted as follow: temperature (60 °C); time of reaction (2 h), steering (600 rpm) and the oil molar ratio was fixed 1:6. Qualitatively, the prepared biodiesel was quantified by GC chromatography, ^{13}C & ^{1}H NMR (Nuclear Magnetic Resonance), AAS and FT-IR spectroscopy. The fuel properties of biodiesel were tested and compared with ASTM D6751 and EN 14214 standards.

1. Introduction

Today with global oil production approaching its peak along with billions of tones carbon emissions into the atmosphere, global temperature rise, threats of climatic changes and the great obstacles to further development of conventional energy sources, it is very important that due attention be given to a range of environmental friendly renewable energy technologies which are too relevant to the developing countries. It is in this context that biodiesel is being recognized as a significant component in many future energy scenarios. Until, recently biodiesel was produced from edible feedstock such as sugar can, maize and other vegetable oils. However, the use of edible feedstock created many problems concerning the food insecurity in most of the under developed countries thus forcing the scientific community worldwide to focus their research efforts to make use of non-edible sources for the production of biodiesel which were not competing with the edible food crops or vegetable oil.

The term biodiesel is defined as “Mono-alkyl ester consisting long chain of carbon derived from various fats of plants and Animals”. In this context, for the production of biodiesel, various type of edible and non edible oil resources have been investigated 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 year for their synthesis [5]. No doubt, various renewable and sustainable resources of energy like solar, wind, geothermal and hydropower, etc. 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 material for biodiesel production, their availability and cost, etc. 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 milk thistle plant. Milk thistle (*Silybum marianum* (L.) Gaert.) shown in Fig. 1 is an annual herb grows up to 15–29 feet, belonging to family Asteraceae. Stem is glabrous or slightly hairy. Leaves are blades up to

* Corresponding author. Tel.: +92 333 9328026.
E-mail address: kifayat.dawar@comsats.edu.pk (K. Ullah).

http://dx.doi.org/10.1016/j.energy.2015.06.028
0360-5442/

Fig. 1. Field Photograph of Milk Thistle plant.

14–50 cm, coarsely lobed margins; cauline leaves brooch, gradually lesser and less divided, bases bristly, curved and auriculate. Phyllary appendages are coming outside, ovate 1–4.1 cm including long pointed spine tips. Corollas are 25.5–30 mm; tubes 12–25.2 mm, throats campanulate about 1.9–3.1 mm. Fruit; the cypselae is black spotted and brown in color, 5.3–8.2 mm as shown in Fig. 2. The composition of milk thistle plant seeds oil show an important source of fatty acids [6].

It grows well in fertile waste land, like on road side and railway tracks. It also grows in an open area having full sunlight. The plant can spread rapidly in disturbed areas and become dominant over another species. It tolerates an annual precipitation up to 532.5 mm and temperature 10–30 °C, respectively. It is native to mediterranean region of Europe. Currently, it is distributed throughout the Southern Europe, North Africa, North America and in the foot of Himalaya, particularly in Nepal, Myanmar, India and Pakistan. It is also distributed in some part of Australia and New Zleand [7].

Oil seed plants have been one of the main feedstock for biofuel production [8]. It is renewable, sustainable and comparable to petro–diesel, reduces overall the global warming up to 78%. In addition, excellent lubricity, outstanding biodegrability, high combustion efficiency and low viscosity are other advantages [8–11].

Fig. 2. Milk Thistle dry seeds sample.

It has been noticed from the survey that yet, systematically, quantitatively and qualitatively no work has been done on milk thistle oil. Attempts have been made to describe the optimized protocol for quantitative production and to qualitatively determine the fatty acid methyl esters profiling for commercialization as compared to petrodiesel. The qualitative and quantitative study of biodiesel fatty acid methyl esters has been the subject of different advanced publications.

However, many questions arise concerning the raw material used for synthesis of biodiesel and its cost. It is only during 2008 the very peaks of the oil spike that biodiesel was able to approach the cost of petro–diesel. Legitimate concerns have also been raised about the possible effect of using vegetable oils for fuel on food prices. Capacity expansion may lead to a decrease in the availability of land for food crops along with the overall negative effect on climate change. The enormous demand for diesel fuel dwarfs the available supply of vegetable oils. The global production of palm, soybean, rapeseed, sunflower, peanut, cottonseed, palm kernel, coconut, linseed, maize, safflower and olive oil (the top 12 vegetable oils) in 2006 was about 1256,00000 metric tons. In contrast, the total consumption of diesel fuel by the transportation industry in the same year was about 6930, 00000 metric tons. Thus, even if all of the vegetable oils produced in the world in 2006 were converted to biodiesel, this would fill only about 18% of the total demand in the same year for the transportation industry alone.

It is necessary that feedstock particularly from non edible oil seeds production must increase dramatically if biodiesel is to have any real positive impact to solve the energy crises and cost issues. The issues of an alternative non edible feedstock has been studied and reviewed recently from several different viewpoints [10]. A considerable amount of research has been conducted on alternative feedstock for biodiesel production mainly using non-edible oils seeds including castor bean, pongame, jatropha, tiger nut oil, safflower, wild safflower etc. However in all these investigations, every effort has been made to make the feedstock acceptable while to best of our knowledge by reviewing literature, no attempt has been made on Milk thistle as an alternative feedstock for biodiesel synthesis and yet not included in the list biodiesel feedstock.

In this research work, the major physico–chemical properties such as kinematics viscosity, density, cloud point, pour point, cold filter plugging point, flash point, sulfur content, cetane value, acid number, calcium, magnesium, sodium and potassium have been studied quantitatively. Various analytical techniques such as Carbon and Proton Nuclear Magnetic Resonance, Gas chromatography, Atomic Absorption spectroscopy and Fourier transfer infrared spectroscopy have been used for their qualitative verification.

2. Materials and methods

The milk thistle plant seeds were collected during several field trips from various part of the country, and washed with soft warm distilled water to remove the dust and impurities. Later on, the seeds were dried in oven at 50 °C till their constant weight. The crude oil was extracted by electric oil expeller (German, KEK P0015-10127) and subsequently organic solvent extraction (soxhlet apparatus), respectively to check out the excet percentage of oil content [12]. Using electrical balance (GF-3000), digital hotplate/stirrer (VWR), thermometer, methanol, chloroform ($CHCl_3$), petroleum ether, *n*-hexane (C_6H_{14}), phenolphthalein ($C_{20}H_{14}O_4$), isopropyl alcohol (C_3H_8O), sulphuric acid (H_2SO_4), anhydrous sodium sulphate (Na_2SO_4), oxalic acid ($C_2H_2O_4$), methyl heptadecanoate