Energy Conversion and Management 171 (2018) 126–132

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Solar energy as a process intensification tool for the biodiesel production from hempseed oil

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A R T I C L E I N F O

Keywords:
Hempseed oil
Biodiesel
Solar energy
Fresnel lens
Energy efficiency

A B S T R A C T

A simple, green, and energy efficient method for the biodiesel production has been developed using Fresnel lens solar concentrator (FSC). The transesterification of hempseed oil using FSC approach and conventional heating approach was studied by varying different process variables such as molar ratio, catalyst loading, reaction time, and stirring speed with an objective to establish benefits of FSC method. The highest biodiesel yield of 97.37% was obtained for FSC method in 4 min of reaction time with reaction conditions of molar ratio 4.5:1, catalyst loading 0.9 wt%, temperature about 60 °C, and 200 rpm. While, conventional heating method yielded only 21.3% of biodiesel in similar reaction conditions. To obtain similar yield (97%), conventional heating method required 70 min of reaction time at molar ratio of 6:1, temperature of 60 °C, catalyst loading of 1.05 wt%, and stirring speed of 300 rpm. Energy efficiency for both the methods was calculated, and observed that FSC method is 73 times more energy efficient than conventional heating method. Therefore, FSC method intensifies the process by reducing the requirements of time, energy, molar ratio and catalyst amount. The physicochemical properties like acid value (0.23 mg of KOH/g of oil), density (0.87 g/cm^3), kinematic viscosity (3.12 mm^2/s), pour point (−1 °C) and flash point (153 °C) of synthesized biodiesel were also compared with American Chemical Society for the Materials (ASTM) D6751 standard and found within the limit.

1. Introduction

Petroleum, derived from fossil fuel is a major source of transportation, which is continuously depleting [1]. Also, use of fossil fuel has adverse effect on the environment as it is responsible for the emission of greenhouse gases [2]. Therefore, recently many countries have started their research in the field of production and utilization of alternative renewable fuel (biofuel) such as bioethanol, biodiesel and biogas. Biodiesel may be one of the good alternatives to the petroleum diesel as it can be used as B100 (100% biodiesel) or as – B6 to B20 (94–80% petroleum diesel blend with biodiesel) in a diesel engine with or without any changes [3]. Biodiesel is fatty acid methyl esters (FAME) produced from the transesterification of the triglyceride with alcohol (methanol or ethanol) or esterification of long chain fatty acid. The sources of triglycerides are edible oils- like sunflower oil, mustered oil, soybean oil, palm oil, coconut oil etc. and non-edible feedstocks – Neem, Jatropha curcas, Karanja, Madhuca indica, Rubber seed, waste cooking oil (WCO), hempseed oil and animal fats [4]. Edible oil cannot be used as feedstock for the commercial production of biodiesel, because it will enhance the production cost and also, compete with the food which cannot afford by developing countries like India. Therefore, the cost effective biodiesel can be produced from the non-edible feedstocks. Recently, industrial hemp (*Cannabis sativa* L.) has been introduced as a non-edible plant oil source because of high contents of triglyceride in its seeds and also it is agricultural by-product [5]. Hemp is a fastest growing woody-herbaceous plant that can grow in wide range of climate condition in all over the world [6]. It is cultivated for its fibers which have a variety of application in textile, paper and construction industries. Industrial hemp newly recognized as an energy crop for the production of bioethanol and biodiesel due to the presence of high amount of biomass and oil seeds [7]. So far, very few reports have been available for biodiesel synthesis using hempseed oil.

In general, transesterification of edible or non-edible oil is performed using conventional method [8,9]. But, in recent time various intensification techniques like microwave irradiation [10–12], cavitation [13–16], supercritical [17], etc. were applied to intensify the biodiesel synthesis process. In all this technique required a considerable amount of energy for heating as well as for intensification, which directly affects the production cost of the biodiesel. Therefore, there is a need for cost effective energy source which not only acts as a heating medium but also intensifies the process. This energy source can be solar energy which is available in abundance all over the world. Solar energy

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https://doi.org/10.1016/j.enconman.2018.05.050
Received 21 February 2018; Received in revised form 20 April 2018; Accepted 14 May 2018
0196-8904/

is a clean, sustainable and renewable source of energy [18]. India has an average 250–300 clear sunny days out of 365 days and average incident solar radiation is an around 4–7 kWh/m^2 per day [19]. Hence, utilization of solar energy as a heating cum process intensification tool for biodiesel production can be an economically viable and greener approach.

Some of the researchers utilized the solar energy as a heating medium for biodiesel production. Agee et al. [20] investigated the transesterification of soybean oil using solar reflector and reported 95% yield in the 60 min of reaction time. Similarly, Tabah et al. [21] also used the direct sun light for the biodiesel production from canola, soybean and WCO and reported the maximum yield of 97.4, 97.2, and 98.6% respectively. But there are no reports on the biodiesel production using Fresnel lens solar concentrator as a direct heating source. Fresnel lens solar concentrator is a series of tiny prism arranged next to each other along the inner surface while it has smooth convex outer surface. It can concentrate solar radiation from wider angles to a common point with high energy density. It is light in weight and cheaply available [22].

The main aim of the present work was to utilize the solar energy as a process intensification tool. Also, the novelty of the study is FSC assisted biodiesel production from hempseed oil. The efficacy of biodiesel production from FSC method was also tested by comparing it with the conventional heating method. The process variables like molar ratio, catalyst loading, reaction time, and stirring speed were optimized for both the methods. Energy efficacy is one of the most imperative parameters for cost effective biodiesel production. Therefore, energy efficacy was also calculated and compared with the conventional heating method.

2. Materials and methods

2.1. Materials

Hempseed oil was procured from the A.G. Industries, Noida, Uttar Pradesh (India). The fatty acid composition and physical properties like acid value, density, viscosity and saponification value were measured and listed in Table 1. Methanol, potassium hydroxide, and anhydrous sodium sulfate (AR grade) were purchased from the SDFCL, Mumbai. Whereas, Acetonitrile and acetone (HPLC grade) were procured from TBCPL, Mumbai. FAME standards – methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate were purchased from Sigma-Aldrich, India.

2.2. Experimental procedure

Biodiesel synthesis from transesterification of hempseed oil was performed using FSC as well as the conventional heating method to check the efficiency of the developed process. In FSC method, reaction parameters such as reaction time (0–5 min), catalyst concentration (0.3–1.05 wt%), molar ratio (3:1 to 5:1), and stirring speed (0–300 rpm) were studied. Similarly, for conventional heating method, reaction time (0–80 min), stirring speed (0–400 rpm), molar ratio (3:1 to 6:1), and catalyst concentration (0.3–1.2 wt%) were studied to get maximum yield.

Table 1
Properties and fatty acid composition of hempseed oil.

Properties	Value
Saponification value (mg of KOH/g of oil)	190.3
Acid value (mg of KOH/g of oil)	1.9
Density (g/cm^3)	0.91
Viscosity (mm^2/s)	31.16
Fatty acid composition	
Palmitic acid (%)	7.12
Stearic acid (%)	3.98
Oleic acid (%)	12.62
Linoleic acid (%)	56.27
Linolenic acid (%)	20.01

2.2.1. Fresnel lens solar concentrator method

The FSC set-up used for transesterification reaction is shown in the Fig. 1. It consisted of Fresnel lens attached on the rigid support and 100 mL three neck round bottom flask (RBF) placed at a point where the maximum concentrated beam of light was felled i.e. at the focal point. All the experiments were performed in a month of April between 12 PM and 2 PM as the solar radiation flux density (W/m^2) was found to be maximum during this period as shown in the Table 2. From the Table 2 it has been observed that biodiesel production is also feasible in other months and at different period of times. The solar radiation flux density was measured using Pyranometer (Dynalab weathertech Pvt. Ltd. Pune, India). Initially, 31.5 g of hempseed oil was transferred in the RBF and irradiated with FSC for 5–6 min to reach about 60 °C temperature. Then 6.56 mL of methanol and 0.28 g of catalyst (KOH) were added under continuous agitation to start the reaction. The aliquot was collected at a regular interval of time. The collected aliquots were washed with distilled water to remove methanol, glycerol and traces of the catalyst. Finally, anhydrous sodium sulfate was added to remove trace of water in the aliquot and analyzed using HPLC (High performance liquid chromatography) to monitor the yield of the reaction. All the experiments were repeated thrice and the average value of HPLC results have been depicted in the Figs.

2.2.2. Convention heating method

Initially, 30 g of hempseed oil was charged in 100 mL three neck RBF and heated using hotplate magnetic stirrer to 60 °C temperature. Then 0.31 g of the catalyst was dissolved in 8.32 mL of methanol and transfer to preheated oil under constant stirring condition. The aliquots were withdrawn at fixed interval of time and treated as mentioned in Section 2.2.1 for the HPLC analysis.

2.3. Analysis

The acid value and saponification value was determined by using titrimetric method [23]. The molecular weight of the hempseed oil was obtained from saponification and acid value as described in our earlier work [13]. Gas chromatography–mass spectrometry (GCMS-QP2010) technique was used for the fatty acid composition determination of hempseed oil in the form of FAME. The separation of fatty acid methyl esters was performed on capillary column Rtx-5Sil MS (25 m × 0.25 m with 0.25 μm thickness). Helium was used as carrier gas with flow rate of 1.5 mL/min. Temperature of injector and detector was set at 230 °C. The oven temperature was programmed initially at 80 °C for 2 min, and heated up to 230 °C at the rate of 20 °C/min. An aliquot of 0.2 μL in hexane was injected with split ratio of 1:50. The MS was set to scan in the range of m/z 40–700.

The progress of the reaction was monitored using HPLC analysis technique (Jasco RI-2031 plus with C-18 column). The isocratic method was applied to analyze the sample using acetonitrile and acetone mixture as a mobile phase in the ratio 70:30 with 1 mL/min flow rate. A typical HPLC chromatogram of hempseed oil methyl ester has been shown in the Fig. 2.

$$\text{Yield of biodiesel (FAME)} = \frac{\text{Total weight of methyl esters}}{\text{Total weight of hempseed oil used}}$$

2.4. Statistical analysis

Statistical analysis is a very important tool for interpreting and summarizing the experimental data. The obtained experimental results