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Rubber seed oil as a potential source for biodiesel production in Bangladesh

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ABSTRACT

In the present paper, rubber seed oil (RSO) has been investigated as a potential source for biodiesel production in Bangladesh. Rubber seed oil has been extracted from the rubber seeds collected from the local garden. Different methods have been applied for the oil extraction, such as mechanical press with and without solvent and cold percolation. Maximum oil content of 49% has been found by mechanical press with periodic addition of solvent. The physico-chemical properties of the oil have been investigated. Effect of seed storage time on free fatty acid (FFA) content of the oil is studied an it is found that the FFA content increases from 2 wt.% (fresh seed) to 45 wt.% after 2 months of storage at room temperature. Biodiesel has been prepared using a three-step method comprises with saponification of oil, acidification of the soap and esterification of FFA. Overall yield of FFA from RSO is found to be around 86%. The final step is esterification that produces fatty acid methyl ester (FAME). The effect of methanol to oil ratio and catalyst content has been investigated for esterification reaction. ^{1}H NMR spectrum of the RSO and biodiesel samples are analyzed which confirms the conversion of RSO to biodiesel. The biodiesel properties have been investigated and are found to be comparable with diesel.

1. Introduction

It is now one of the most important considerations with respect to the world present crisis and demand of fuel consumption and production of it from crude. Besides this greenhouse gas emission due to the excess use of petroleum leads to the global warming which is now in the significant phase of consideration, because the unfavorable atmosphere is approaching day by day. To meet the crisis alternative fuel sources are being developed around the globe, such as biodiesel, bioalcohol, biomass, biogas and synthetic fuels. Among them biodiesel can be used directly in the diesel engine, while others need some sort of modification before they are used as substitute of conventional fuels [1,2]. Depending upon the climate and soil conditions, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. For example, soyabean oil in the US, rapeseed and sunflower oils in Europe, palm oil in South-east Asia (mainly Malaysia and Indonesia) and coconut oil in the Philippines are being considered [3]. Currently, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials – the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long-term. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel. The use of non-edible oils when compared with edible oils is very significant in developing countries because of the tremendous demand for edible oils as food, and they are far too expensive to be used as fuel at present [4,5]. Recently the planning commission of India has recommended Karanja and Jatropha for biodiesel production in India [6].

Bangladesh's per capita energy consumption is very low, the lowest within the Indian subcontinent. Total primary energy consumption in 2004 was 30.70 MTOE and the energy consumption mix was estimated as: indigenous biomass 60%, indigenous natural gas 27.45%, imported oil 11.89%, imported coal 0.44% and hydro 0.23% [7]. The energy potential of biodiesel resources has not been assessed in Bangladesh. Approximate land use for agriculture is 54.5% and forests are 17.6% of total land area of the country [7]. Around 91.8 thousand hectare of land of Bangladesh (14.7% of the total planted forest area) is used for rubber plantation [8] from where the rubber seeds can be collected. The productivity of Rubber seed oil per hectare per annum is reported as 217 kg oil/ha [9]. Taking the data as a basis, the expected annual rubber seed oil production in Bangladesh is ~0.02 million MT. Moreover additional rubber plantation can be carried out in the unused lands, which accounts around 0.32 million hectare [10]. As a potential feedstock, rubber seed oil will add an additional value of energy to the

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original latex value of rubber plants. Recently, the production of biodiesel from refined (FFA free) rubber seed oil by transesterification reaction with methanol using poly(sodium acrylate) supporting NaOH as a water-resistant catalyst has been reported [11]. The main difficulty to produce biodiesel from the crude rubber seed oil is the high free fatty acid (FFA) content in the oil which is approximately 18% as reported by Ramadash et al. [9]. Many pretreatment methods have been proposed for reducing the high FFA content of the oils, including steam distillation, extraction by alcohol and esterification by acid-catalysis [12–15]. However, steam distillation for reducing high FFA requires a high temperature and has low efficiency. Because of the limited solubility of FFAs in alcohol, extraction by alcohol method needs a large amount of solvent and the process is complicated [14]. Compared with the two former methods, esterification by acid-catalysis makes the best use of the FFA in the oil and transforms it into biodiesel [15]. The catalysts can be homogeneous acid-catalysts (usually sulfuric acid) or solid acid-catalysts [16,17]. Compared with the homogeneous catalyzed process, solid acid-catalysts offer some advantages for eliminating separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower [14].

Ramadash et al. [9] reported the production of biodiesel from rubber seed oil by two-step method where FFA were converted to biodiesel by homogeneous acid-catalyzed esterification followed by base catalyzed transesterification of the dried oil. However, if the acid value of the oils or fats is very high, esterification in a single step may not reduce the FFA efficiently because of the high content of water produced during the reaction [18]. In this case, a mixture of alcohol and sulfuric acid can be added into the oils or fats three times (three-step pre-esterification) and after each step of esterification the water needs to be removed.

In the present paper, rubber seed oil has been extracted from the kernel of the seed by different methods, such as mechanical press with and without solvent and cold percolation method. A three-step method has been studied for biodiesel production from RSO. In this method, FFA is produced from oil by saponification followed by acidification and finally, FFA is converted to fatty acid methyl ester (FAME) by acid catalyzed esterification with methanol. The properties of the RSO and biodiesel, such as specific gravity, viscosity, iodine value, pour point, flash point and calorific value are measured.

2. Materials and methods

2.1. Chemicals

Methanol (99–100%), ethanol (99–100%), sodium hydroxide pellets (96%), potassium hydroxide pellets (>84%), phenolphthalein (pH 8.2–9.8), starch, acetone (99%), sodiumthiosulfate (99.0%), n-hexane (96%), ethanol (99.8%), hydrochloric acid (37%), sulfuric acid (98%), isopropanol, iodine, sodium iodide, glacial acetic acid and bromine. were purchased from Merck, Germany. All the chemicals used were analytical reagent grade.

2.2. Primary seed properties and extraction of oil

A number of rubber seed samples were collected from different locations. The seed kernel was separated and weighted to measure the seed to kernel ratio. Rubber seed, a brown colored seed weighted from 2.68 to 5.04 g bears a kernel varies from 1.53 g to 3.00 g of weight which was 53.74–68.35% of the seed. However average wt.% of the kernel is 58.83%.

Different methods were used to extract oil from the seed. The first method was mechanical press, a vertical, manual operated, cylindrical (4.3 cm ID) mechanical press was constructed which have a spiral screw that convey the mass from the hoper to pressure raising area. Slow and continuous rotation of the press allowed raising sufficient pressure for the extraction of oil. The spiral screw was used for random mixing and size distribution. Oil drainage nozzles are located in the face of the expeller. Cold percolation process is another method for oil extraction in which a batch of crushed rubber seed kernel was emerged in the solvent in various conditions. Hexane was used as a solvent. The solvent to seed ratio (wt./wt.) was optimized and the total oil content by this method was determined. Mechanical press with periodic addition of the solvent has been used for oil extraction and seed/solvent ratio is optimized.

2.3. Biodiesel preparation from RSO

The raw rubber seed oil was saponified, acidified and esterified sequentially. In the first step; saponification, a small batch of 50 g oil was taken in a three-necked round bottom flax (500 mL) with a vertical condenser and placed on a plate heater with magnetic stirrer (Model: HB502). Temperature was maintained 68–70 °C. Different stoichiometric amounts of alcoholic sodium hydroxide solution (oil/alcholic NaOH is 1:3, 1:4, 1:6) were added to the oil and heated under reflux with vigorous stirring. The reaction was completed in 30 min and stopped by cooling the reaction volume. The unconsumed NaOH was titrated with HCl solution. The conversion of the saponification reaction was calculated from following

$$X = \frac{3r + 2N_0 a}{9N_0} \quad (1)$$

where r – number of moles of NaOH consumed; N_0 – initial moles of oil; a – mol.% of FFA in oil.

After saponification, the following second step is acidification in which the soap solutions were treated with different stoichiometric amount of hydrochloric acid. The reaction was fast and completed within 5 min. After the reaction, FFA was separated from the top layer and FFA content was determined by titrimetric method. Yield of FFA from oil is calculated using the following

$$Y_{FFA} = \frac{V \times M \times M_{FFA}}{w} \quad (2)$$

where V – volume of NaOH solution (L); M – molarity of the NaOH solution; M_{FFA} – molecular weight of FFA (g/mol); w – weight of the oil sample (g).

In the final step, the FFA was converted to FAME by acid catalyzed esterification reaction with methanol. Reactions were carried out at 60 °C and atmospheric pressure. Typically, 50 g FFA was put into a three-necked 250 mL round bottomed flask equipped with a reflux condenser and rubber septum. The flask was immersed in an oil bath with a temperature controller and magnetic stirrer preheated to required temperature. Required amount of sulfuric acid was mixed with methanol and transferred into the reaction medium with syringe. Samples were withdrawn in every 10 min and FFA content was analyzed. After 100 min when the FFA content reduced to <1% the contents were cooled to room temperature, and reaction product was washed with water (200 mL). The organic phase was collected and dried under vacuum (40 mm Hg) at 100 °C for 20 min. Effect of oil/methanol ratio and catalyst concentration was investigated.

2.4. Analytical methods for oil and biodiesel

FFA in the oil and biodiesel samples was analyzed by the method described in AOCS Aa 6-38 [19]. To determine FFA of sample, 4–5 g of samples were dispersed in isopropanol (75 mL) and hexane (15 mL) followed by titration against 0.25 N NaOH solution. Saponification value (SV) was determined by standard method