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Production of biodiesel from low priced, renewable and abundant date seed oil

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ABSTRACT

The present work is definitely an approach towards attaining price competency of bio-diesel to petroleum diesel. The oils extracted from abundantly available waste of Zahidi, Basra and Khazravi date seeds were used to produce biodiesel using acid (HCl), base (KOH), immobilized enzyme (lipase), immobilized enzyme/acid (lipase/HCl) and immobilized enzyme/base (lipase/KOH) catalyzed processes. Mixed catalysis (immobilized enzyme + acid or immobilized enzyme + base) resulted in better yields in comparison to acid or base catalysis. The properties of biodiesel were evaluated by fuel standard tests and the results were compared with EN14214 and ASTM D6751 standards. Biodiesel produced from date seed oil was found to have a high cetane number (55–60.3), low iodine value (44–50) and good flash point (135–140 °C). Pour point of pure biodiesel produced from Khazravi and Zahidi was found to range from 2 to −2 °C. Biodiesel produced from Basra exhibited good pour point (−4.7 to −8.3 °C) in comparison to other varieties. The components present in biodiesel produced from various date varieties were determined by gas chromatographic-mass spectrometric analyses (GCMS). The fatty acid (%) detected in date seed biodiesel were oleic acid (33.4–47.4), lauric acid (19–28), palmitic acid (13.6–19.2), myristic acid (13.6–17.44) and linoleic acid (6.4–8.5). A special feature of date seed oil biodiesel was the presence of considerable amounts of low chain fatty acids.

1. Introduction

The exploitation of various sources as alternative fuels is in high focus due to the increasing threat of depletion of fossil fuel reservoir and adverse effects on environment. Among the alternative sources, biodiesel is an important and promising resource [8]. Both the major problems, depletion of fossil fuel reservoir and environmental issues, can be tackled by the use of biodiesel as a transport fuel. Biodiesel is an alternative energy source of petrodiesel with comparable quality and is being used in diesel engine as a fuel without or with little modification. Chemically, biodiesel is made of methyl esters of fatty acid (FAME) obtained by the transesterification reaction of alcohol and vegetable oil extracted from different plants.

Biodiesel is a renewable energy source having many advantages to be used as an automobile fuel. Biodiesel is less polluting than petroleum diesel as it lacks sulfur and very low in carbon dioxide emissions and thus ultimately helps in decreasing global warming and depletion of fossil fuel reservoir [9]. Another advantage of biodiesel fuel is its blending capacity with other energy resources. The lubricating property of the biodiesel may extend the lifetime of engines. The main hurdle for the commercialization for biodiesel is the high cost of feedstock for the biodiesel production. About 75% of the total cost of biodiesel production is of feedstock used as a raw material [20,22]. Therefore, it would be imperative to spot low cost feedstock as a raw material for the biodiesel-production, which could be helpful in the reduction of cost of biodiesel and increasing its commercial value. Use of non-edible vegetable oil for the biodiesel production is one of the promising solutions as it does not value for the human consumption.

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Date palm or *Phoenix dactylifera* seed comprises 6.10%–11.47% weight of the total date fruit, which is a waste product of many date processing industries [7]. Date seeds are burden as solid waste except a little amount is used as a feed for the animals like poultry, camel, sheep and cattle [2]. Huge amounts of date seeds can be collected from date processing plants and industries directly or indirectly [11]. The composition of date seed is 22.5–80.2% dietary fiber, 3.1–7.1% moisture, 2.3–6.4% protein, 0.9–1.8% ash and 5.0–13.2% fat [1]. Fatty acids found in date seed oil are lauric acid (13%–25.8%), palmitic acid (6%–13%), oleic acid (11.9%–58.8%) and myristic acid (7% and 13%) [3,4,5]. This combination of fatty acids of date seed oil offers the use of date seed oil for the biodiesel-production [10]. The date palm chiefly found in the hot region of arid (southwestern Asia) and northern Africa. According to the statistical report of FAO, 7.85 million tons of dates were produced in 2010. Top ten date producing countries including Egypt (13,52,950 tons), Saudi Arabia (10,78,300 tons), Iran (10,23,130 tons), United Arab Emirates (U.A.E) (7,75,000 tons), Pakistan (7,59,200 tons), Algeria (7,10,000 tons), Sudan (4,31,000 tons), Iraq (5,66,829 tons), Oman (2,76,400 tons) and Libya (1,61,000 tons) contributes about 91% to the total world date production [16]. In the light of FAO, 2010 mentioned statistics, it was estimated that 4,79,304 to 9,03,314 tons of date seeds containing 9% of oil contents was produced throughout the world out of which only a small amount is currently being used for different purposes [18].

In the current research date seeds were used as a low cost feedstock for biodiesel-production. This research work not only aims towards introducing a low cost feedstock for biodiesel production but also to describe the use of multi-catalysis processes for biodiesel production and, the assessment of biodiesel quality by following standard methods.

2. Materials and methods

2.1. Materials

Date palm seeds of three different varieties (Khadravi, Zahidi and Basri) were collected from the local market of Faisalabad, Pakistan. Potassium hydroxide, Hydrochloric acid, Lipase enzyme, Methanol, Calcium chloride, Sodium alginate, Potassium hydrogen phosphate and dipotassium hydrogen phosphate used in the present study were of analytical grade and purchased from Merck.

2.2. Extraction of oil and immobilization of lipase

Healthy seeds of date were washed, sun dried and grounded into a powder of uniform particle size of 1 mm using a heavy duty grinding mill. Date seeds oil was extracted from grounded seeds using hexane. Extracted date seed oil was purified using a vacuum Rotary evaporator at 40 °C and −760 mmHg. Lipase was immobilized into calcium alginate beads by mixing 1 g of lipase into 1 g of sodium alginate dissolved in 100 ml of water. This mixture was subsequently introduced by using narrow tip burette into 0.1M calcium chloride solution to form calcium alginate beads (0.35 mm).

2.3. Transesterification

The extracted date seed oil was converted into biodiesel and glycerol (by-product) by catalytic transesterification with methanol. Transesterification process was carried out by acid (HCl), base (KOH) and enzyme (lipase) catalysts as well as using enzyme catalysis followed by acid or base catalysis. Three concentration levels of each catalyst (acid, base and enzyme) were selected to optimize biodiesel yield. Acid catalyzed transesterification reaction was performed at three concentrations levels (in volume) of 25%, 50% and 100% HCl compared to date seed oil. For example, 100% HCl means equal volume to date seed oil. Transesterification experiments were conducted in triplicate at said concentrations levels of HCl using 10 g of date seed oil and 60 g methanol. The mixture of oil, methanol and catalyst was stirred at 60 °C for 90 min. Base catalyzed transesterification reaction was carried out using KOH (0.125%, 0.25% and 0.50% KOH compared to oil weight). The required concentration of KOH was mixed with 10 g of date seed oil and 3 g of methanol. The mixture of oil, methanol and catalyst was stirred at 60 °C for 90 min. Enzyme catalyzed transesterification reaction was done at three different concentration levels including 3%, 4% and 5% of lipase (lipex, Novazyme, Denmark) compared to date seed oil. The varied concentrations of lipase immobilized on calcium alginate beads were mixed with 10 g of date seed oil and 50 g of methanol under constant refluxing at 40 °C for 10 h. Biodiesel was also produced using mixed catalysis by using immobilized lipase/acid (2% immobilized lipase + 15% HCl, 2.5% immobilized lipase + 30% HCl, 3% immobilized lipase + 45% HCl) and immobilized lipase/base (2% immobilized lipase + 0.05% KOH, 2.5% immobilized lipase + 0.1% KOH, 3% immobilized lipase + 0.15% KOH) systems at three concentration levels. The produced biodiesel was washed with excessive quantities of hot distilled water (80 °C) to remove the excess methanol from the biodiesel. All experimental trails were triplicated.

2.4. Determination of fuel properties

Fatty acid composition of methyl esters was determined by gas chromatographic mass spectrometric (GC-MS) analysis. GC-MS analyses were performed using a Perkin Elmer Clarus 600 GC System, fitted with an Elite-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; maximum temperature, 350 °C), coupled to a Perkin Elmer Clarus 600C MS. Ultra-high purity helium (99.99%) was used as carrier gas at a constant flow of 0.2 ml/min. The injection, transfer line and ion source temperatures were 220, 200 and 200 °C, respectively. The ionizing energy was 70 eV. Electron multiplier (EM) voltage was obtained from autotune. All data were obtained by collecting the full-scan mass spectra within the scan range 10–600 m/z. The injected sample volume was 0.1 μl with a split ratio of 50:1. The oven temperature program was 35 °C hold for 10 min, 10 °C/min 200 °C hold for 10 min. The unknown compounds were identified by comparing the spectra obtained with mass spectrum libraries (NIST 2011 v.2.3 and Wiley, 9th edition).

The pH of biodiesel was tested using Hanna pH meter (model, HI 8010). Density (g/ml) of all biodiesel samples was determined by weighing the mass of 1 ml of each sample. Specific gravity of biodiesel was measured by standard specific gravity bottle. For determination of iodine value 0.1 g of biodiesel was taken in glass stoppered iodine flask of 250 ml capacity. The oil was dissolved in 20 ml of carbon tetrachloride and 25 ml of Wijs solution. The contents of the flask were vigorously shaken and placed in the dark for 30 min. Then 20 ml of 15% potassium iodide solution as added followed by the addition of 100 ml of distilled water. The contents were then titrated against 0.1 N $Na_2S_2O_3.5H_2O$ using starch as indicator until yellow iodine color was disappeared. Same procedure was repeated using blank solution. Iodine value (IV) was calculated using following formula (eq. (1)):

$$\text{I.V} = (\text{Sample titration} - \text{Blank titration}) \times \text{Normality of } Na_2S_2O_3.5H_2O \times 12/\text{sample wt.(gm)} \times 100 \quad (1)$$

Saponification value of biodiesel was determined by taking 0.5 g