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Reactive extraction of castor seeds and storage stability characteristics of produced biodiesel

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ABSTRACT

In the present study, oil was extracted from a single castor seed by eppendorf vial method, and the oil yield was compared with the yield obtained from Soxhlet method. The oil yield from both methods was about 55% and comparable. Free Fatty Acid (FFA) content of extracted castor oil was found to be lower (<1 mg KOH/g oil). Therefore, single step transesterification (reactive extraction) was carried out to study the effect of various reaction variables on the conversion of castor oil biodiesel. The optimum biodiesel conversion of ~93% was achieved under following conditions: 4 h, 1:250 oil to MeOH molar ratio, 1 wt.% NaOH, 40 °C, 0.75 mm particle size, 20 g seed, 600 rpm and 10 (vol.%) co-solvent. The estimated fuel properties of biodiesel obtained with NaOH, KOH and NaOH (with co-solvent) were found to be similar and within the limits of ASTM standards. Similarly, storage stability of prepared biodiesel was evaluated over a six-month storage period (180 days) under three different storage conditions. The results showed a sharp decrease in fuel stability over time in terms of increase in density from 0.878 to 0.984 g/cm^3, kinematic viscosity (10.59–16.18 cSt), acid value (0.52–5.15 mg KOH/g) respectively. While, iodine value significantly decreased from 82.5 to 54.57 g I_2/100 g oil over time. Biodiesel sample stored in the open air degraded faster than samples stored in other storage conditions.

1. Introduction

At present, most of the energy needs of the world are met through petrochemical sources like coal, petroleum and natural gas (Passos et al., 2009). As increasing demand for fossil fuels, depletion of its reserves and environment pollution has led interest towards alternative bio fuels (Pradhan et al., 2012). Biodiesel is an alternative fuel for transportation, which can be produced from animal fat, vegetable oil (edible or non-edible) or waste cooking oil. It is renewable, environmental friendly and also gives fewer pollutants compared to fossil fuels (Hincapie et al., 2011). Biodiesel production from edible or non-edible oil includes several steps such as oil extraction, refining (degumming, deacidification, dewaxing, dephosphorization, dehydration) followed by transesterification. These multiple processes for oil refining include 70% of the total cost of biodiesel production when refined oil is used as feedstock (Zakaria and Harvey, 2012; Lian et al., 2012). As a substitute, transesterification can be carried out directly from oil bearing materials without prior extraction which is termed as "reactive extraction" or "in situ transesterification". It is a simplification of biodiesel production process and at the same time reduces the production and feed stock cost considerably (Zakaria and Harvey, 2012). This process involves alcohol as an extracting solvent and at the same time transesterification reagent. Elimination of a costly oil extraction process before the transesterification is possible by reactive extraction, which reduces the capital cost (Kasim and Harvey, 2011), biodiesel cost, process time and solvent amount (Pradhan et al., 2012). The non-edible oil seeds used so far in reactive extraction include rape seed (Zakaria and Harvey, 2012), castor (Pradhan et al., 2012; Hincapie et al., 2011), jatropha (Kasim and Harvey, 2011) and karanja (Porwal et al., 2012). Among the non-edible oil seeds, castor is a promising feed stock to produce biodiesel due to its positive aspects like cheap, non-edible, resistant to grow in drought conditions and was cultivated mainly in India (Madankar et al., 2013). The detailed information about the conditions required for castor plantation, applications and its oil yield comparison with various oil seeds was reported elsewhere (Dasari and Goud, 2013, 2014). As the reports on reactive extraction are scanty, it is necessary to explore alternate raw materials and ways to reduce production costs of biodiesel.

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Methanol is the most commonly used solvent in reactive extraction compared to ethanol due to its low-cost (Porwal et al., 2012). The amount of catalyst required is depended upon the acid value of oil (Orta et al., 2012). Generally, catalysts used for the reactive extraction include enzyme/acid/alkali catalyst. The limited availability and the high cost of enzymes are preventing their usage as the catalyst (Borges et al., 2011). For reactive extraction, alkali catalyst is favourable than the acid catalyst due to its higher reaction rate at lower temperatures (Borges et al., 2011).

Even though, the usage of biodiesel has several increasing ecological and health benefits (Yang et al., 2013), deterioration of biodiesel is more severe compared to commercial petro-diesel during storage (Ndana et al., 2012). Thus, the storage stability is a major concern about the flourishing commercialization of biodiesel in the fuel market. Storage stability is the capacity of fuel to oppose changes in its physicochemical characteristics brought by contact with its surroundings (Mazumdar et al., 2013). The destabilization of fuel happens in terms of thermal or oxidative or storage stability mechanisms (Natarajan, 2012). The problem of biodiesel deterioration during storage is due to various factors such as the temperature, unsaturation content, moisture content, microbial contamination, light, metal, nature of the container and nature of fatty acid composition of parent oil. There are several reports available in the literature about the effect of storage stability on various parameters of biodiesel (Ndana et al., 2012; Mazumdar et al., 2013).

Most of the storage stability studies reported in the literature includes an effect of different antioxidants on oxidative stability by using Rancimat method (widely) and by other methods such as Petro OXY method and the pressurized differential scanning calorimetric method; while few studies include the change in various properties (acid value, viscosity, peroxide value) of biodiesel during a short or long-term storage period.

From aforementioned discussion, it was clear that, there is no report in the literature on the optimization of various reaction variables in reactive extraction of castor seeds, particularly with "NaOH" as a catalyst. Moreover, no proper information is available on the storage stability of castor oil biodiesel under different storage conditions. Hence, the present report aimed at to investigate the effect of various parameters on reactive extraction with NaOH as catalyst due to its low-cost and further to study the long term storage stability of castor oil biodiesel under three different storage conditions.

2. Materials and methods

2.1. Castor seeds

Castor seeds were purchased from a local market in Anantapur, Andhra Pradesh, India. The seeds were stored in dark and air tight condition to prevent photo-oxidation and moisture adsorption.

2.1.1. Pre-treatment and preparation of castor seeds

Castor seeds were cleaned manually and heated at 50 °C in an oven for 24 h. Pre-treated seeds were cooled to room temperature and used in the reactive extraction. Whole castor seeds (shell and kernel) were utilized in the experiments. The seeds were crushed to the average particle size of 1 mm using a mixer grinder. Pre-treatment of seeds was followed based on the results achieved in the previous study reported elsewhere (Dasari and Goud, 2014).

2.2. Chemicals and reagents

Analytical grade methanol (99% pure), NaOH (>97%), Phenolphthalein indicator, sodium thiosulphate pentahydrate, starch, Wij's solution and ethanol were purchased from Merck, India Ltd. Pellets of KOH (>85%) were procured from Ranbaxy Fine Chemicals Ltd., India and carbon tetra chloride was obtained from S. D. Fine Chemicals Ltd., India.

2.3. Vial extraction method (using single seed)

Oil was extracted from the castor seed by vial method. Vial extraction method was carried out using a single castor seed and two 2 ml eppendorf vials. From the available seed samples, randomly single castor seed was selected and the weight of the seed was noted. Kernel was grinded manually with a mortar and pestle. The grinded kernel was divided into two halves and transferred into pre weighed two 2 ml eppendorf vials. 2 ml hexane was added to each vial and centrifuged at 10,000 rpm for 20 min. The supernatant was decanted into other two 2 ml pre-weighed eppendorf vials and placed in a fume hood with the lid open in order to evaporate the solvent. An additional 2 ml of hexane was added to the precipitated grinded seed in each vial and the whole process was repeated. The procedure for preliminary tests was followed according to reported literature (Vaknin et al., 2011). The oil content of castor seed in the present study was compared with that of Soxhlet method reported elsewhere. The oil content (Soxhlet method) and acid value of extracted oil were determined according to the procedure described previously (Dasari and Goud, 2014).

2.4. Reactive extraction

Reactive extraction of castor seeds was carried out in a three-neck 250 ml round bottom flask equipped with a reflux system, magnetic stirrer, heater and placed in an oil bath (Fig. 1). Initially, sodium methoxide solution was prepared by dissolving a known amount of NaOH in methanol and heated to desired temperature. When solution reached the desired temperature, 20 g of macerated castor seed material was transferred into the reaction vessel and then mixing (200–600 rpm) was started. Thus the reaction was carried out for the desired

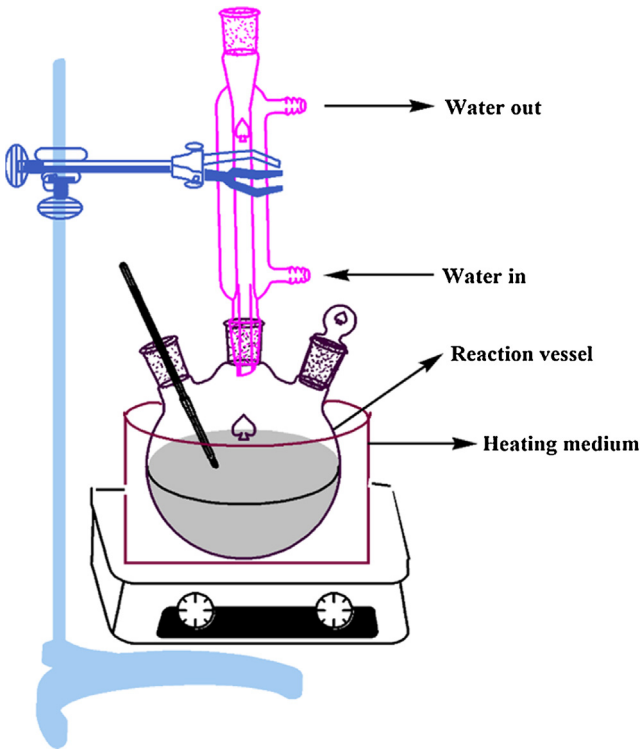

Fig. 1 – Schematic diagram of reactive extraction set up.