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Hybrid biofuels from non-edible oils: A comparative standpoint with corresponding biodiesel

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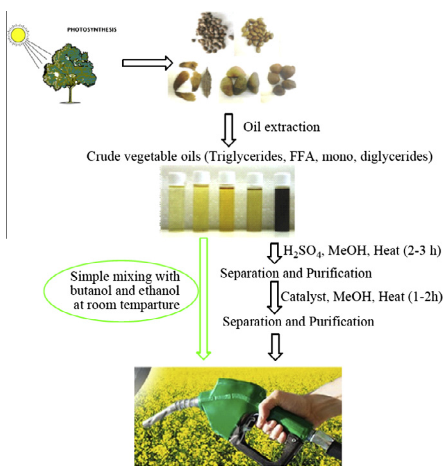
HIGHLIGHTS

- Non-edible oil based hybrid biofuels.
- Natural surfactant based hybrid fuel systems (FFA, mono, diglycerides).
- Improved cold flow properties in comparison to corresponding biodiesel.
- Future energy utilities.

GRAPHICAL ABSTRACT



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ABSTRACT

Exploration of new non-edible feedstocks for biofuel production and the use of economically favorable conversion technologies could significantly contribute to bioenergy research. In this regard the present investigation aims to highlighten hybrid biofuels (HBFs) prepared from crude vegetable oils of five locally available plant species namely, *Gmelina arborea* Roxb (GAO), *Mimusops elengi* Linn (MEO), *Acer laurinum* Hasskarl (ALO), *Thevetia peruviana* Schum (TPO) and *Mesua ferrea* Linn (MFO). This new approach does not involve any chemical reactions and can substantially reduce the production cost of vegetable oil based biofuels. Besides, the HBF systems prepared here can be 100% renewable as they only contain vegetable oil, butanol and ethanol, all products derived from biomass. The naturally occurring mono-, di-glycerides and free fatty acid (FFA)s in crude vegetable oils (or esters in pretreated oils) functioned as surfactants in the formulation of stable fuel systems. The fuel properties of the formulations were affected by the concentrations of these compounds in the vegetable oil. The optimum formulations (oil:butanol:ethanol ratio of 60:30:10) exhibited viscosity (4.7–5.4 mm^2/s), density (0.86–0.88 gm/cm^3) and gross calorific values (38.91–39.18 MJ/kg) comparable with their corresponding fatty acid methyl esters (FAMEs). Moreover, they show superior cold flow properties than FAMEs. The present investigation

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suggests that non-edible oil based HBF systems formulated in the study containing 'bio-based' and 'green' surface active agents in the system offers economically attractive candidature for the future biofuel industry.

1. Introduction

Due to increasing concerns over fossil fuels utilization, the use of vegetable oils for production of biofuels has gained significant importance in recent years. But the major impediments in successful commercialization of vegetable oil based biofuels like biodiesel are high feedstock cost (accounting for nearly 80% of the total cost) and conversion technology needed to reduce viscosity. Nevertheless, the right choice of raw materials as well as the method for production of vegetable oil based transportation fuels must always rely on techno-economical aspects. With the global demand for renewable biofuel gearing up, the exploration of feedstock for production of biofuels is both essential and critical. The judicious exploitation of newer non-edible feedstock is imperative which will undeniably serve as an incremental step for addressing the long recognized problem of energy supply and simultaneously also support further research endeavors related to green chemistry, feedstock biology and bioenergy research [1,2]. The use of vegetable oils as fuel is not new. Idea of using vegetable oils as fuel dates from the days of the diesel engine. However, their use thus far has been restricted by inherently higher viscosity. The high viscosity of crude vegetable oil reduces fuel atomization and increases penetration which in turn contributes to the formation of engine deposits, piston ring sticking, injector coking, and thickening of oil. Several methods are there to reduce the viscosity of vegetable oils such as dilution (blending), microemulsification, pyrolysis (thermal cracking), and transesterification [3–6]. Among these approaches transesterification is the most sought after process for reducing viscosity of vegetable oils. However, requirement of longer reaction time, high energy input during biodiesel purification steps, and formation of by-product in the form of glycerol makes the whole process expensive, time consuming, labor intensive and economically less attractive. In addition biodiesel is plagued by storage fouling, poor cold flow properties and increased NOx emission in comparison to petrodiesel [7].

A viable alternative approach which can reduce process economics in this regard can be the mixing/blending of vegetable oil or diesel with polar low molecular weight alcohols, in presence of surface active agents (surfactants and co-surfactants) to improve miscibility of polar and non polar oil phases. The process sufficiently reduces the interfacial tension between the dispersed or polar phase (e.g. ethanol) and continuous (oil) phases, resulting in formation of hybrid biofuel (HBF) having physicochemical properties comparable to diesel and biodiesel (Scheme 1) [7–10]. Due to the similarities of HBFs with microemulsions, this type of biofuel production method has also been termed as microemulsification. Microemulsion systems can be characterized by well dispersed optically isotropic nano-sized fluid structures or colloidal dispersions [4,11]. Though water has been predominantly used as polar phase for the formation of microemulsion, recent studies have also shown successful application of ethanol as polar phase for formulating hybrid fuel systems having aforementioned structural similarities with 'microemulsions' [3,7,24]. The advantages of this approach over the transesterification include lower production costs, short production time, simple and easy implementation (on the farm blending) and no by-product formation due to non-involvement of chemical reactions. Besides, such fuels incorporating alcohols exhibit lower combustion temperature, which causes drastic reduction in the emissions of thermal NO_x, CO, black smoke and particulate matter [8–11]. Microemulsions are classified in terms of Winsor system of classification and the same could also be extended to the HBFs due to their obvious structural similarities [7]. Formulation of microemulsions are greatly influenced by the properties of surface active agents and they are the 'key components' which play the most crucial role in converting the system from one Winsor type to another. Generally, the most ideal systems of HBFs formulations are the Winsor Type IV, a single phase system in which the polar (water or alcohol or aqueous alcohol) phase is completely dispersed in reverse micelles occurring in the oil phase. On the other hand, the systems are classified as Winsor Type II (a two phase system) if the polar phase is not completely dispersed in the oil continuum [3–17].

Steady development in this area of fuel research has been witnessed in current years. However, still there is paucity of scientific information pertaining to vegetable oil based HBFs (many dating back to 1980–1990s). Most of these studies dealt with either 'alcohol-diesel-surfactant system' or 'alcohol-vegetable oil–diesel-surfactant systems'. Although, such fuel formations exhibit properties comparable/superior to diesel, but in reality these complex systems do not confer to the broad objectives of biofuel research owing to use of non renewable components and hazardous surface active agents. These complex systems comprising mixtures of different externally added surface active agents increase the cost of fuel preparation. Besides, their use in engines may also contribute to corrosion problems and green house gas (GHG) emission [18]. Some of the NOx/SOx producing surface active agents used in previous studies include: 2-amino-2-methyl-l-propanol, ethoxylated mono- and di-nonylphenols [19], N.N-dimethylethanolamine [19], triethyl amine [15], trialkylamine [9], sodium bis-2-ethylhexyl sulfosuccinate [20], sodium 2-(2-dodecyloxyethoxy)ethyl sulfate and coconut fatty acids diethanolamide [21], dodecylamine [22], sodium bis(2-ethyl) dihexyl sulfosuccinate [23], oleyl amine [24], 2-ethylhexylnitrate [24].

Considering the disadvantages like corrosion and GHG emissions, the use of 'bio-based' surface active agents free from sulfur, nitrogen, inorganics and acids must be given preference for HBF formulation [18]. Consequently, research on eco-friendly surfactant based microemulsions and HBFs has gained importance in recent years. Sorbitan monooleate, alcohol ethoxylate (hydrophobic), polyisobutylene succinic anhydride ester of monomethyl-capped poly(ethylene glycol) [25], glycerin and polyethoxy-ester based surfactants [14], butanol [26–29] are some of the examples of such non-polluting surface active agents used for formulating eco-friendly microemulsion fuels. However, there exists scope for further improvement through cost effective and environmentally benign HBF preparation using vegetable oil and 'bio-based' surface active agents may be an attractive fuel option in the ensuing future.

The presented research work investigates the feasibility of non-edible oil based HBF as an economically attractive alternative to biodiesel. We report the formulation of a simple and cost effective HBF system comprising of 'crude vegetable oil–butanol–ethanol' which can be produced entirely from biomass sources (Scheme 1). The reported work also specifically highlightens the role of mono-, di-glycerides and FFAs (or fatty esters) present in the crude vegetable oils as naturally occurring surfactants for the formulation