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Optimization of biodiesel production from palm oil under supercritical ethanol conditions using hexane as co-solvent: A response surface methodology approach

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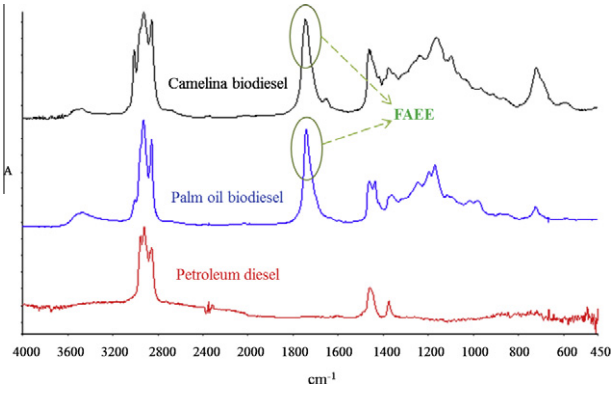
HIGHLIGHTS

- Conversion of palm oil to ethyl esters at supercritical ethanol conditions.
- Hexane as a co-solvent to accelerate the transesterification process.
- Ethyl esters analyzed with GC–MS, FT-IR, and TGA.
- A response surface methodology to design and optimize the conversion process.

GRAPHICAL ABSTRACT

Overlay of FTIR spectra of palm oil biodiesel, camelina biodiesel and petroleum diesel fuel.



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ABSTRACT

In the present work, response surface methodology (RSM) was used to optimize the biodiesel production from palm oil under supercritical ethanol conditions. Hexane was added as a co-solvent, which in turn accelerated the reaction rate and increased the biodiesel yield. This process enables simultaneous transesterification of triglycerides and ethyl esterification of fatty acids in a shorter reaction time and may reduce the energy consumption due to simplified separation and purification steps. Different process parameters including alcohol to oil molar ratio (25:1–50:1), reaction time (10–30 min), reaction temperature (260–300 °C) and co-solvent ratio (0.1–0.4% v/v) were optimized using response surface methodology. A mathematical model was developed for predicting the fatty acid ethyl ester (FAEE) yield. Fatty acid ethyl esters produced from palm oil were measured and analyzed using FT-IR, GC–MS and thermogravimetric analysis (TGA) methods. The fuel properties of the biodiesel produced were determined and compared to the American society for testing and materials (ASTMs) standards for biodiesel.

1. Introduction

The rise of the petroleum prices in the world market and the depletion of fossil resources have increased the interest in renewable fuels. One of the renewable alternatives is vegetable oil fuel, which is popularly known as biodiesel. Biodiesel is a renewable, nontoxic, biodegradable, and eco-friendly fuel consisting of fatty acid alkyl esters (FAAEs) obtained from renewable sources like vegetable oils and animal fats [1–3]. Biodiesel is advantageous than regular petroleum based diesel fuel in terms of sulfur content, flash point, aromatic content, and cetane number [4]. The usage of

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biodiesel can reduce the emissions of SO_x, CO, particulate matter, and hydrocarbons in the exhaust gas compared to the regular diesel fuel [5,6].

Recently, vegetable oil fuels are becoming more attractive because of their renewability, energy security and due to their high-energy content which is close to that of petroleum based fuels [7–9]. The properties of biodiesel are similar to that of regular diesel fuel, and can be used as a fuel blend or as a substitute for diesel fuel [6,10,11]. Nowadays different vegetable oils such as soybean, rapeseed, camelina, palm, and sunflower oils are being used for the production of biodiesel. Among all the potential oil sources for the production of biodiesel, palm is one of the most abundant oils in the world with a high yield of 4.2 tons ha^{-1} $year^{-1}$ and is economical [12,13]. Palm oil accounts for one third of the total oil production in the world, and requires a very small land area compared to that of other oil crops [14]. Several methods like dilution [15], microemulsions [16], pyrolysis [17], catalytic cracking [18] and transesterification [16,19] can be employed to produce biodiesel from vegetable oils. Out of all the conversion processes, transesterification is the most economical and simplest way to produce biodiesel [3,20]. This process provides a fuel with physical characteristics close to that of regular diesel fuel, with little or no deposits when used in diesel engines [5,20]. Transesterification is a process in which the triglycerides present in the vegetable oils chemically react with alcohol to produce alkyl esters and glycerol with the aid of catalyst. Based on the type of catalyst used in the transesterification, this process was categorized into alkali, acid and enzyme catalytic processes. The alkali process gives a high purity and high yield of biodiesel in a short span of reaction time but is not suitable for oils with high free fatty acid (FFA) content [21]. For such kinds of oils acid esterification followed by alkali transesterification can be employed to reduce the high FFA content and to improve the biodiesel yield [9]. However, the longer reaction time and low catalyst recovery are problems with this process [22]. Enzyme catalytic transesterification requires longer reaction times [16]. To overcome these limitations, Saka and Demirbas proposed a different route to produce biodiesel from vegetable oil. In this process biodiesel can be produced via non-catalytic transesterification under supercritical alcohol conditions [23,24].

In the non-catalytic transesterification via supercritical alcohol method, the alcohol esterification of high free fatty acids and the transesterification of triglycerides into alkyl esters occur simultaneously without using catalyst. This process enables simultaneous transesterification of triglycerides and ethyl esterification of fatty acids in a shorter reaction time and may reduce the energy consumption due to simplified separation and purification steps. The catalytic transesterification processes requires less amount of alcohol (1:9 oil to alcohol ratio), and mild temperatures (60 °C) for the production of biodiesel compared to that of non-catalytic supercritical transesterification (1:45 oil to alcohol ratio, 300 °C temperature, and 100 bar pressure), but catalyst separation and the limitation of feedstock are disadvantages [3,9]. Various alcohols such as methanol, ethanol, propanol, butanol and amyl alcohol can be used for the transesterification. Ethanol is preferred because it is renewable, non-toxic, eco-friendly and can be produced from agricultural resources [25–27]. Also, ethanol having high dissolving properties for oil is a good extraction solvent. Ethanol under super critical conditions, acts as both a reactant and an acid catalyst [28].

Apart from the advantages like rate enhancement, increased yield, and improved purity from the supercritical process it has some drawbacks like high equipment cost and high energy consumption due to high temperature and pressure conditions. This limits the supercritical transesterification process to be viable for large scale industrial applications [29]. However, the introduction of co-solvents like hexane, carbon dioxide, and calcium oxide into the reaction mixture decreases the severity of the reaction parameters and can make this process practical. The addition of co-solvents can decrease the critical point of alcohol and allow the supercritical reactions to be carried out at milder temperatures [30–33]. Our previous studies have shown increased yield when hexane was added as co-solvent in the transesterification of camelina sativa oil under supercritical ethanol conditions [3]. The co-solvent in the reaction mixture can increase the mutual solubility of the oil and alcohol at lower reaction temperatures and accelerates the reaction rate at supercritical conditions [22].

The objective of the present study is to optimize and evaluate the influence of different process parameters on the biodiesel yield from supercritical transesterification of palm oil using response surface methodology. Different process parameters including alcohol to oil molar ratio (25:1–50:1), reaction time (10–30 min), reaction temperature (260–300 °C), and co-solvent ratio (0.1–0.4% v/v) were optimized using response surface methodology. Pressure was maintained above supercritical conditions of ethanol (63 bar). A mathematical model was developed for predicting the fatty acid ethyl ester (FAEE) yield. The biodiesel produced is analyzed using Gas Chromatography-Mass Spectroscopy (GC–MS), thermogravimetric analysis (TGA) and Fourier Transform and Infrared Spectroscopy (FT-IR) and fuel properties of palm oil biodiesel have been discussed in detail.

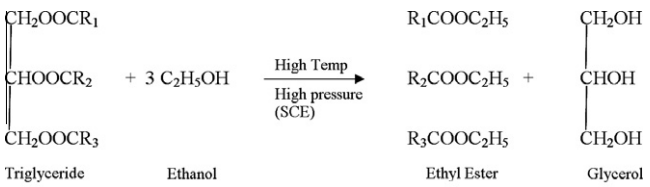
2. Experimental section

2.1. Materials and methods

Organic certified palm fruit oil (biological source: Elaeis guineensis) was purchased from Sigma Aldrich, Saint Louis, MO, USA. Absolute ethanol was procured from Pharmaco-AAPER and commercial alcohols, Brookfield, CT. HPLC grade n-hexane and aniline were obtained from Acros organics, New Jersey. The supercritical ethanol process was carried out in a 100 mL bench top PARR 4593 Micro reactor with a 4843-controller (Parr Instrument Company, Illinois, USA). The Instrument can be operated up to 350 °C and 120bars.

2.2. Transesterification of palm oil

The transesterification reaction of palm oil under supercritical condition is given in Fig. 1. The crude palm oil mainly consists of 93–95% triglycerides and 2.3–6.7% free fatty acids (FFA's) [34,35]. In the supercritical state, the intermolecular hydrogen bonding in the ethanol molecule will be significantly decreased. As a result, the polarity and dielectric constant of ethanol are reduced allowing it to act as a free monomer. Ethanol at supercritical conditions can solvate the triglycerides to form a single phase of vegetable oil/ethanol mixture and yield fatty acid ethyl ester and diglycerides. Further, diglyceride is transesterified to form ethyl ester and monoglyceride, which is then converted into ethyl ester and glycerol in the last step.



R_1, R_2 and R_3 are long chain hydrocarbons which may be same or different.

Fig. 1. Transesterification reaction at supercritical ethanol conditions.