



Fatty acid methyl esters synthesis from non-edible vegetable oils using supercritical methanol and methyl *tert*-butyl ether



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ABSTRACT

Fatty acid methyl esters (FAMES) are useful as biodiesel and have environmental benefits compared to conventional diesel. In this study, these esters were synthesized non-catalytically from non-edible vegetable oils: neem oil and mahua oil with two different methylating agents: methanol and methyl *tert*-butyl ether (MTBE). The effects of temperature, pressure, time and molar ratio on the conversion of triglycerides were studied. The temperature was varied in the range of 523–723 K with molar ratios upto 50:1 and a reaction time of upto 150 min. Conversion of neem and mahua oil to FAMES with supercritical methanol was found to be 83% in 15 min and 99% in 10 min, respectively at 698 K. Further, a conversion of 46% of mahua oil and 59% of neem oil was obtained in 15 min at 723 K using supercritical MTBE. The rate constants evaluated using pseudo first order reaction kinetics were in the range of 4.7×10^{-6} to $1.0 \times 10^{-3} \text{ s}^{-1}$ for the investigated range of temperatures. The activation energies obtained were in the range of 62–113 kJ/mol for the reaction systems investigated. The supercritical synthesis was found to be superior to the catalytic synthesis of the corresponding FAMES.

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1. Introduction

The rate of depletion of fossil fuels increases correspondingly with our energy requirements. The disparity between production and consumption is ever widening. This necessitates the need to develop alternative fuels that can be renewably obtained. Bioethanol and biodiesel that constitute the majority of the biofuels today are viable and safer alternatives to fossil fuels. These can be renewably sourced from plants, animals and microorganisms [1–4]. Biodiesel is a fast growing industry, with a proven 15-fold increase in global biodiesel production compared to a 4-fold in case of bioethanol since 2004 [5]. It is gaining increased global visibility, promotion and acceptance because of good performance and enhanced environmental benefits [6–9]. Biodiesel is chemically a mixture of fatty acid methyl esters (FAMES) possessing similar properties as that of diesel. One of the major sources for production of these esters is vegetable oil because of its easy availability, biodegradability and low sulphur and aromatic content. However, it has several drawbacks like higher viscosity, lower volatility and hydrolytic stability [6]. Thus, different methods have been employed for FAMES production to overcome these problems of vegetable oils like thermal cracking, micro-emulsions, blending

of pure vegetable oil with diesel and the most commonly used method i.e., transesterification [10].

Transesterification is a method of converting vegetable oil into alkyl esters with or without catalyst using acyl acceptors such as alcohols, esters and ethers. Alkaline catalysts such as NaOH or KOH are mostly used because of high conversions and relatively low operation cost [11,12]. Further, when the feedstock oil is having high concentration of free fatty acids (>1%) and moisture (>0.5%), acid catalyzed transesterification is preferred as it will inhibit the saponification reaction and will lead to the higher yield of esters [13,14]. Acid or base catalyzed synthesis of FAMES has disadvantages such as the formation of soap in case of alkaline catalyzed synthesis and, corrosion and longer reaction time in case of acid catalyzed reaction. A greener alternative using enzymes is accompanied with low yield of alkyl esters, longer reaction time and limited feedstock variability [15–20].

Supercritical fluid technologies for FAMES synthesis obviate the need of a catalyst. Supercritical fluids are fluids above their critical point that have intermediate properties to gases and liquids. These fluids have good solvating power that can be tuned by changing both the pressure and temperature [21,22]. Methanol is the most commonly used reagent for the transesterification reaction because it is cheap and highly reactive, as it is a short chain alcohol [6]. Supercritical conditions ($T_c > 513 \text{ K}$ and $P_c > 7.8 \text{ MPa}$) ensure liquid like densities and gas like diffusivities [23]. Other acyl

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acceptors such as esters, dialkyl carbonates and ethers have also been investigated for FAMES synthesis [24–26]. The supercritical pathway for FAMES or biodiesel synthesis precludes pretreatment steps for free fatty acid and water removal, as it is practically independent of feedstock compositions [27,28]. Further, the downstream processing is highly simplified in comparison to the catalytic route of FAMES synthesis. The catalytic route of synthesis requires high production cost because of the pretreatment of feedstock for removal of free fatty acids and water and for the purification of the product mixture. It involves several steps of washing the product mixture with water to obtain the desired esters. For example, catalytic synthesis of biodiesel from the rapeseed oil using KOH required longer times to obtain two clear phases of esters and glycerol [29]. However, only evaporation of alcohol is required in case of supercritical synthesis to obtain FAMES and purified glycerol. Further, high conversions of FAMES are obtained in a short span of time (5–60 min) at supercritical conditions because of simultaneous esterification of free fatty acids and transesterification of the triglycerides [29–31]. Thus, the higher capital cost of the supercritical pathway because of high pressure can be compensated by the same productivity in small reactors at a faster rate [32]. Therefore, the non-catalytic pathway for FAMES synthesis has been investigated for some non-edible vegetable oils such as Jatropa, Karanja, castor and rubber seed oil using different acyl acceptors [33].

Non-edible oil plants/trees are plentiful in developing countries and can be a potential renewable source for FAMES synthesis [10,34,35]. Two such non-edible oils (neem and mahua) have been investigated in the present study for FAMES synthesis. Neem tree (*Azadirachta indica*) grows in tropical and semitropical regions of many Asian countries like India, Bangladesh, Sri Lanka, Burma, Malaysia, Pakistan and Cuba and Mahua tree (*Madhuca indica*) grows mainly in India. Seed and kernel of neem and mahua tree contains about 20–30 wt% and 40–50 wt% and, 35–50 wt% and 50 wt% of oil, respectively. Neem oil yield is around 2670 kg oil/hectare, and a yield of 800 kg/hectare after a decade can be expected from the mahua tree [36]. Thus the reactants chosen for the transesterification reaction are neem and mahua oil along with methanol and MTBE as methylating agents.

Short chain alcohols like methanol and ethanol have been extensively studied for the FAMES or biodiesel synthesis using conventional and non-catalytic route. It has been observed that methanolysis always gives higher yields in comparison to ethanolysis under supercritical conditions for the similar reaction time [20,37]. Thus methanol was preferably considered as one of the reagent for the present study. The reaction products obtained from the transesterification reaction include FAMES and glycerol. Several methods have been developed to address the over production of glycerol, by utilizing it in specific reactions [38,39]. Using dimethyl carbonate, methyl acetate and *tert*-butyl methyl ether as methylating agents, glyceryl derivatives such as glycerol carbonate (from dimethyl carbonate), triacetin (from methyl acetate) and glycerol *tert*-butyl ether (GTBE) (from MTBE) are obtained [24]. The transesterification of canola oil using MTBE resulted in high yields of FAMES when MTBE was used a reagent in comparison to methyl acetate and dimethyl carbonate [40]. Thus, MTBE was chosen as another methylating agent for the present study.

The objectives of this study were threefold: (a) to synthesize FAMES from neem and mahua oil by transesterification using supercritical methanol and MTBE, (b) to understand the effect of important parameters that affect the conversion of triglycerides to FAMES such as reaction time, temperature, pressure and initial molar ratio and (c) to compare the conversions, rate constants and activation energies from both the oils and the reagents.

2. Experimental section

2.1. Materials

Neem and mahua oils, which were extracted by the cold-pressing from their respective seeds, were provided by Biofuel Development Board at Gandhi Krishi Vigyana Kendra (GKVK), Bangalore. Methyl *tert*-butyl ether (CAS no. 1634-04-4) with purity (>99% GC) was procured from TCI chemicals, Japan. Methanol and *n*-heptane with purity (>99.99% GC) were obtained from Merck Chemicals and butyl laurate with purity (>99% GC) was supplied by Sigma Aldrich, Bangalore. The solvents, ethers and alcohols, were used without any further purification. However, the oils were heat homogenized (to melt separated fat) and vacuum filtered through Whatman filter paper (150–200 mesh) to obtain clear oil free from any solid impurities.

2.2. Methods

All the reactions were carried out in an 11 ml stainless steel (SS-316) batch reactor. The reactor was placed in a furnace equipped with a PID controller for a precise temperature control within ± 1 °C. The mixture of oil and methanol or MTBE was loaded in the reactor leading to different global densities (ratio of total mass of the reactants and the volume of the reactor). Thus, for a particular initial molar ratio, temperature and pressure, the amount of reactants to be loaded was calculated using these global densities obtained at the operating conditions by using a combination of PR-EOS and LB mixing rules. This methodology is similar to other reports that have used isochoric method to synthesize esters [41] and biodiesel from different vegetable oils [20,28,29,31,42]. The calculations require mixture critical properties and operating conditions: temperature, pressure and molar ratio. Thus, the pure component critical properties of methanol and MTBE were obtained from NIST fluid property database. However, due to thermal decomposition of triglycerides at higher temperatures, the critical properties of these triglycerides (tripalmitin, tristearin, triolein and trilinolein) were calculated using Constantinou and Gani group contribution technique [43] as discussed in an earlier report [44]. Further, the critical properties of oil (mixture of triglycerides) were also calculated using the LB mixing rule.

After suitable reaction time, the reactor was quenched in an ice bath to stop the reaction. The product mixture was evaporated (at 363 K for 15 min) to remove excess methylating agent to obtain a mixture of esters and unreacted oil after centrifugation to separate glycerol. The supernatant was diluted suitably in *n*-heptane and spiked with 20 μ L of *n*-butyl laurate as internal standard (IS) to prepare samples to be analyzed using gas chromatography (GC). Several reactions were performed in triplicates and the variation in conversion was within 2%. The reactions occurring with the reagents (methanol and MTBE) are shown in Scheme 1.

2.3. Analysis

The fatty acid composition of oils was determined by GC–MS. The oil samples were first derivatized to fatty acid methyl esters (FAMES) for the fatty acid analysis by a base catalyzed followed by the acid catalyzed method. Approximately 0.15 g of oil sample was taken in a 15 ml screw-cap test tube for the derivatization and 2 ml of *n*-hexane was added to it. 1 ml of 2 M methanolic KOH solution was added to the mixture and the tube was closed and vigorously shaken for 30 s. It was then heated in a water bath at 343 K for 2 min. After that 1.2 ml of 1 M HCl was added to the solution and was gently

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