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A comparative study of direct transesterification of camelina oil under supercritical methanol, ethanol and 1-butanol conditions

Yingqiang Sun [a], Harvind K. Reddy [a], Tapaswy Muppaneni [a], Sundaravadivelnathan Ponnusamy [a], Prafulla D. Patil [a], Changzhu Li [b], Lijuan Jiang [c], Shuguang Deng [a,b,*]

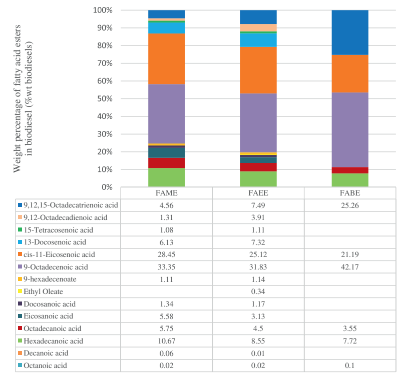
[a] *Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, USA*
[b] *Hunan Academy of Forestry, Changsha 410004, China*
[c] *Central South University of Forestry and Technology, Changsha 410004, China*

HIGHLIGHTS

- Comparison of transesterification of camelina oil under supercritical methanol, ethanol and 1-butanol conditions.
- Characterization of fatty acid methyl esters, ethyl esters and butyl esters.
- Chemical composition of fatty acid methyl esters, ethyl esters and butyl esters.
- Effect of different alcohols on biodiesel yields.

GRAPHICAL ABSTRACT

Chemical compositions of FAME, FAEE, and FABE.



	FAME	FAEE	FABE
■ 9,12,15-Octadecatrienoic acid	4.56	7.49	25.26
■ 9,12-Octadecadienoic acid	1.31	3.91	
■ 15-Tetracosenoic acid	1.08	1.11	
■ 13-Docosenoic acid	6.13	7.32	
■ cis-11-Eicosenoic acid	28.45	25.12	21.19
■ 9-Octadecenoic acid	33.35	31.83	42.17
■ 9-hexadecenoate	1.11	1.14	
■ Ethyl Oleate		0.34	
■ Docosanoic acid	1.34	1.17	
■ Eicosanoic acid	5.58	3.13	
■ Octadecanoic acid	5.75	4.5	3.55
■ Hexadecanoic acid	10.67	8.55	7.72
■ Decanoic acid	0.06	0.01	
■ Octanoic acid	0.02	0.02	0.1

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ABSTRACT

Transesterifications of camelina oil under supercritical methanol, ethanol, and 1-butanol conditions are investigated and compared to find the suitable alcohols for the esters conversion process. The factors affecting the yields of fatty acid methyl esters (FAME), fatty acid ethyl esters (FAEE), and fatty acid butyl eaters (FABE), such as reaction temperature and time, are studied and discussed in detail. The increase of the reaction temperature and time is proved to be favorable to the production of FAME, FAEE, and FABE initially since the transesterification is a reversible, endothermal reaction; however, the persistent increase of reaction temperature and time will decrease the yield of the *Camelina sativa* biofuels due to their thermal instability. The composition and thermal stability of biodiesel produced under various supercritical alcohol conditions are characterized by gas chromatography-mass spectrometry and thermogravimetric analysis methods. The saturated degree of fatty acid esters in *C. sativa* oil decreases with the increase of the alkyl chain of the alcohols from methanol, ethanol, to 1-butanol. The physical properties of biodiesels including the specific gravity, viscosity, calorific value, cold properties, and cetane number are tested and compared with the American Society for Testing and Materials (ASTM) standards. According to the results, the specific gravity and the viscosity of the *C. sativa* biodiesels are comparable to the ASTM standards. The calorific value, cetane number, and cold properties of biodiesel are improved

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[*] Corresponding author at: Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, USA. Tel.: +1 575 646 4346; fax: +1 575 646 7706.

E-mail address: sdeng@nmsu.edu (S. Deng).

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with the increase of the length of the carbon chain of alcohols, while they decrease with the increase of unsaturated degree of compositions of biodiesels.

1. Introduction

With the predicted exhaustion of fossil fuel supplies and the increasing emissions of greenhouse gases (GHG) [1–3], research related to hydrogen adsorption [4] and other kinds of green energy has been studied in detail. Biodiesel, is a sustainable, non-toxic, biodegradable fuel, and has some environmental benefits [5–8]. In addition, biodiesel is easy to store, transport, and use in current diesel engines without any modifications [6].

Biodiesel, as a promising alternation of regular diesel, is a renewable diesel fuel consisting of alkyl esters. It can be obtained from vegetable oils, waste cooking oils, algae and animal fats [9]. Vegetable oil is attractive since it is renewable, environmental friendly, locally produced and high-energy content [7,9,10]. *Camelina sativa* is primarily described as a weed in the United States although it is well known as an underutilized oil seed [11]. However, compared with other kinds of vegetable oil resources, *C. sativa* being a lower-input crop with a higher yield, is easier to collect without centrifugation and freezing, and has higher net energy ratio characteristics [12]. It can be cultured on land that is unsuitable for food production in cold weather conditions, which avoids the negative implications on food security [7,13]. Also, *C. sativa oil* is rich in Omega-3 fatty acids [10], leading to the positive energy balance for biodiesel production, which the reported the net energy ratio is 1.47 [12,13].

Supercritical fluids treatments can decrease the value of the solubility parameter of methanol/ethanol. The dielectric constant of alcohols dramatically changes and becomes closer to that of vegetable oils under supercritical conditions and form a homogeneous mixture [14]. Transesterifications of camelina oil with supercritical alcohols are proved to be the simplest, green, and economical route to produce biodiesel. Furthermore, transesterification of the oil with short carbon chain alcohols is the most promising solution to the high viscosity problem [15]. Therefore, much of the effort has been focused on the transesterification of vegetable oils in supercritical and subcritical alcohols, including methanol [16,17], ethanol [17–19]. The factors, such as heating methods including conventional and microwave [20], co-solvents including water [19], hexane [7], acetone and toluene [21], benzene [22], catalysts such as homogeneous and heterogeneous [9,20,23] catalysts have been studied exhaustively. It is worth mentioning that the reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols has been investigated in detail [24]. However, the compositions of fatty acid methanol esters (FAME), fatty acid ethanol esters (FAEE), and fatty acid 1-butanol esters (FABE), and the influences of compositions on the physical properties of biodiesels have not been studied. In addition, as fossil fuels are limited, research related to finding alternatively renewable fuels with both high net energy ratio and excellent physical properties should be considered.

Based on the previous work related to the production of FAME and FAEE from camelina oil, the preparation of fatty acid butyl esters using *C. sativa* oil under supercritical conditions is processed and reported in the other work. In this work, FAME, FAEE and FABE are prepared and characterized by GC–MS and TGA analysis methods. Secondly, the effect of the varied alcohol reactants on compositions of related biodiesels have been reported and compared. Thirdly, the effect of temperature and time on yields of FAME, FAEE and FABE have been studied. And finally, physical properties of biodiesels have been tested and compared, and the influences of compositions and the length of alkyl chains of alcohols on physical properties have been discussed in detail.

2. Experimental

2.1. Materials and methods

Expeller-pressed unrefined *C. sativa* oil is purchased from mountain-rose herbs, Eugene, OR. Methanol (⩾99.9%, v/v), ethanol (⩾99.5%, v/v), and 1-butanol (⩾99.4%, v/v), directly used alcohols, were all purchased from Sigma–Aldrich for the transesterifications with *C. sativa* oil. The transesterifications of *C. sativa* oil with supercritical alcohols were carried out in the PARR 4593 Micro-reactor with a 4843-controller (Parr Instrument Company, Illinois, USA). After removal of unreacted alcohols in the products by vacuum oven, thermo-gravimetric analysis (TGA) of camelina oil and camelina biodiesels were performed using Perkin Elmer Pyris 1 TGA. *N*-hexane (⩾99.5%, GC) was used as the solvent for GC–MS analysis.

2.2. Transesterifications of camelina oil with supercritical alcohols

The transesterifications of camelina oil consisting of 98.3% triglycerides (TGAs) with supercritical methanol, ethanol, and 1-butanol are simulated in Fig. 1. The reactor was initially pressurized to 500 psi (3.45 Mpa) by injection of inert gas N_2 in all the experiments at room temperature in all the experiments. More than the stoichiometry amounts of alcohols were used to shift the equilibrium to the proposed production side since the transesterification reaction was a reversible reaction. In this paper, reactions were processed with the same molar ratio of camelina oil: alcohol of 1:40 for 60 min at 290 °C to study the compositions of FAME, FAEE, and FABE. For the investigation of the influences of temperature and time on the yields of biodiesels, the experimental plan for methanol and ethanol involved five levels of temperature: 245 °C, 275 °C, 290 °C, 300 °C, 310 °C; three levels of temperature for 1-butanol: 290, 300, 310; and the reaction time varied from 5 min to 60 min with five levels.

2.3. Analytical methods

For the quantification of reaction products, the camelina biodiesel samples were analyzed by an Agilent 7890A gas chromatograph (GC) incorporated with an Agilent 5975 series mass selective detector (MSD) GC–MS system with a capillary column (DB-23, 60 m × 250 μm × 0.15 μm nominal). The contents of biodiesels were calculated quantitatively by internal standard method. Methyl tricosanoate (C23:0, 99%), purchase from Sigma Aldrich, is used as the internal standard for the quantification of the compositions of fatty acid butyl esters. Approximately, 1 μL sample was injected into the gas chromatograph with helium as the carrier gas. The injection was performed in split mode (10:1). The parameters of the oven temperature program consisted of: starting at 50 °C with 10 °C/min intervals up to 220 °C (1 min) and up to 250 °C with 5 °C/min intervals (2 min). The temperature of the injector and detector were set at 250 °C. The gas chromatogram