Energy Conversion and Management 101 (2015) 402–409

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Transesterification of camelina sativa oil with supercritical alcohol mixtures

Yingqiang Sun [a,b], Sundaravadivelnathan Ponnusamy [b], Tapaswy Muppaneni [b], Harvind K. Reddy [b], Jun Wang [b], Zheling Zeng [a], Shuguang Deng [a,b,*]

[a] Department of Chemical Engineering, Nanchang University, Nanchang 330031, China
[b] Department of Chemical & Materials Engineering, New Mexico State University, Las Cruces, NM 88003, USA

ARTICLE INFO

Article history:
Received 5 February 2015
Accepted 26 May 2015

Keywords:
Camelina sativa oil
Biodiesel
Alcohol mixtures
Transesterification
Supercritical conversion

ABSTRACT

The transesterification of camelina sativa oil with methanol–1-butanol, and ethanol–1-butanol alcohol mixtures under supercritical conditions have been studied in order to maximize biodiesel yield and improve biodiesel quality. The influence of the variation of the molar ratio of methanol–1-butanol and ethanol–1-butanol from 1:0, 3:1, 2:1, 1:1, 1:2, to 0:1 on the yield of free fatty methyl esters/free fatty ethanol esters–free fatty acid butyl esters, the composition of the biodiesel blend mixtures, and the physical properties of the biodiesel have been investigated at the reaction temperature of 290 °C, reaction time of 30 min, and the initial reaction pressure of 500 psi. A maximum yield of 86.14 wt% for free fatty acid methyl esters–free fatty acid butyl esters with the optimum cold property can be obtained at the molar ratio of methanol–1-butanol of 0.5–0.9. Also, a maximum yield of 85.60 wt% for free fatty ethyl esters–free fatty butyl esters with the lowest pour point can be achieved at the molar ratio of ethanol–1-butanol in the range of 0.5–0.7.

1. Introduction

With the increase of rapid industrialization and population, the energy demands are going to increase from 13.95 terawatt presently to 50 terawatt at the end of this century [1]. The increasing energy demand, petroleum prices, and growing concerns over climate change call for the development of alternative renewable energy sources, such as wind, solar, and biomass [2]. The prospective and problems of renewable energy strategies for sustainable development have been discussed in detail based on the case of Denmark by Hernrik Lund, and a positive conclusion has been given to convert present energy systems into a 100% renewable energy system [3]. A further study reported the barriers and their solutions of implementation of renewable energy systems in Denmark, which played a representative role in political decision making processes in many countries [4]. It is predicted that biodiesel is going to make up to 80% of the growth in liquid fuels from 2010 to 2035 in the United States [5]. It is well known that vegetable oils, animal fats, and recycled grease, which are rich in triglyceride have a great potential to be suitable for biofuel production under right processing conditions [6]. Biodiesel is an environmental friendly and renewable fuel. It can be produced using self – catalyzed reactive extraction from germinated oilseed [7]. It is also biodegradable, non-toxic, and has high thermal stability, which is stable in the range of 30–150 °C [8]. Also, biodiesel can be used in modern unmodified diesel engines [9]. Therefore, it is a favorable alternative to conventional energy sources, which will help to decrease the release of greenhouse gas [10].

Biodiesel is defined as a fuel composed by mono-alkyl esters of long chain fatty acids from vegetable oils or animal fats [11]. It can be produced by transesterification of short carbon chain alcohol with vegetable oils or animal fats, micro emulsions, and thermal cracking (pyrolysis) [12]. The expensive cost of biodiesel production and competition of food demand with biodiesel production are the limitations for practical use of biodiesel. The right feedstock can significantly reduce the production cost, because of the cost of raw materials accounts for about 60–80% of the total [13]. Camelina, also known as false flax or gold – of – pleasure, has drawn much attention in the study of biofuel due to its low – input property in culture [13]. It was described as a weed in the United States previously [13], however, it is described as second-generation biodiesel feedstock due to its non-edible feature now [14]. Camelina sativa has a relatively shot growing seasons, and

* Corresponding author at: Department of Chemical & 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).

http://dx.doi.org/10.1016/j.enconman.2015.05.056
0196-8904/

can be cultured on relatively poor and saline soils with little nitride fertilizer [13]. It can be cultured in cold and arid regions, which are not suitable for the culture of food crops [15]. Camelina seeds contain > 40% oil on a dry weight basis [13], and its oil is rich in Omega – fatty acid. Therefore, their high net energy ratio property, which is reported 2.2 MJ/MJ in west Canada [16], and about 1.47 MJ/MJ in North America [17], makes it a promise feedstock for biodiesel production.

Transesterification as the simplest and economical route to produce biodiesel with a lower viscosity, has been studied in detail previously. Supercritical transesterification reaction is a high reaction rate, high yield, and high purity process. Factors affecting transesterification of camelina oil have been studied dramatically. Transesterification kinetics of camelina sativa oil under conventional and microwave heating conditions have been studied and compared, and microwave heating was proved to be an efficient method for transesterification [18]. The transesterification reactions under supercritical and subcritical methanol conditions have been compared, and transesterification under supercritical methanol can get higher biodiesel yield than subcritical methanol conditions [19]. A microreactor with T-shaped junction was used as a continuous flow reactor to optimize biodiesel production from soybean oil [20]. The effect of reaction temperature, reaction time, molar ratio of alcohol/oil and co-solvent to oil ratio on ethanolysis of camelina oil with hexane as a co-solvent have also been reported [15]. For the practical use of alkyl esters, methyl and ethyl esters from camelina oil blend with diesel fuel have been evaluated [9]. The effect of heterogeneous metal oxide catalysts, i.e., BaO, SrO, MgO and CaO, on transesterification of camelina oil with methanol have been investigated, and the relative order of efficiency of catalysts was BaO > SrO > CaO > MgO [21]. The catalyzed biodiesel production with new catalysts, such as PA/NaY(PA = organic phosphonic acid), was investigated and optimized [22]. Another work studied KOH modified zirconia as solid base catalyst on biodiesel production from silybum marianum [23]. Hexane as a regular co-solvent for biodiesel production has been studied exhaustively [19]. Carbon dioxide as a co-solvent for biodiesel production from soybean oil has also been reported [24]. The results indicated that hexane and carbon dioxide as co-solvents was favorable to biodiesel yield.

Though lots of studies of parameters of transesterification reactions have been done, however, many problems are still confronted in the research of biodiesel production by supercritical transesterification. Firstly, the cost of equipment for supercritical transesterification and operation fee is high. The high cost of equipment is due to strict requirement of reaction conditions, such as reaction temperature of 260–350 °C [25]. The high supercritical transesterification operation fee is around $42,086,302/yr [25]. Therefore, it is not a viable way for large – scale industrial applications. Secondly, a complete conversion is hard to achieve since transesterification is a reversible reaction [26]. Thirdly, the high pour points of biodiesels from variable feed stocks, such as −12 °C of biodiesel from corn oil [27], lower calorific value, cetane number, and oxidation stability are the intractable problems in the practical use of biodiesel [26].

Biodiesel production through transesterification is usually catalyzed by homogeneous or heterogeneous acid and base catalysts [28]. Supercritical methanol, ethanol, and 1-butanol are supposed to act as both reactants and acid catalysts in transesterification processes [29]. The inductive effect of alkyl groups, and the acidities of alcohols are decreasing with the increase of carbon chains, which lead to the decrease of reactivity of methanol, ethanol to 1-butanol with camelina sativa oil. Also, the thermal stability of fatty acid esters is going to decrease with the increase of the length of alkyl chain of esters. Therefore, the variations of reactivity of alcohols and the thermal stability of fatty acid esters make alcohol mixtures a potential reactant to increase the yield of supercritical transesterification products.

The physical properties of biodiesel, such as cold flow property, acid number, cetane number, calorific value, and oxidative stability are important factors of biodiesel. The composition of biodiesel and minor components, such as water, free glycerin, free fatty acid, and residual alcohols can significantly affect biodiesel properties [30]. The use of alcohol with longer alkyl chain is proved to be favorable to the cold property of biodiesel, which is reported that butyl esters are 10 °C lower than methyl esters, and ethyl esters are 2 °C lower than methyl esters [31].

The main objectives of the current work are to obtain a higher yield of biodiesel with good low-temperature flow property. In this work, transesterification with various supercritical alcohol mixtures have studied and reported in detail. The influence of molar ratio of different alcohol mixtures on transesterification yield have been investigated and reported in this paper. Also, the effect of the variation of the molar ratio of alcohol mixtures on the properties of biodiesel, such as the cetane number, calorific value, and cold property, have been evaluated and presented.

2. Materials and analysis methods

The camelina sativa oil purchased from mountain-rose herbs, Eugene, OR consists of 98.3% triglyceride (TG), and can be used directly for the transesterification with supercritical alcohol mixtures. Methanol (99.9%, v/v), ethanol (⩾99.5%, v/v), and 1-butnaol (⩾99.4%, v/v), directly used alcohols, were all purchased from Sigma–Aldrich for the supercritical transesterification with camelina sativa oil. Since the supercritical temperatures of methanol, ethanol, and 1-butanol are 239 °C, 243–287 °C, separately, the transesterifications of camelina sativa oil with supercritical metha nol/ethanol–1-butanol were carried out at 290 °C for 30 min in the PARR 4593 Micro-reactor with a 4843-controller (Parr Instrument Company, Illinois, USA). Molar ratios of methanol/ethanol: 1-butanol were varied from 1:0, 3:1, 2:1, 1:1, 1:2, to 0:1 for the study of the effect of molar ratios of alcohol mixtures on compositions and physical properties of blend biofuel. After removal of unreacted alcohols remained in the products by vacuum oven, 8 mg of camelina biodiesels was used for thermos-gravimetric analysis (TGA) performed using Perkin Elmer Pyris 1 TGA. Heptane (⩾99.5%, GC) was used as the solvent for gas chromatography–mass spectrometry (GC–MS) analysis. And the composition of the biodiesel obtained was characterized by the GC–MS system (Agilent, USA) incorporated with an Agilent 5975 C MSD (Triple-Axis Detector) and an Agilent 7890 A GC equipped with a capillary column (HP-5 MS, 5% phenyl methyl silox 30 m × 250 μm × 0.25 μm nominal).

2.1. Characteristics of camelina sativa oil

The quality of camelina sativa oil is expressed in terms of the physicochemical properties such as acid value and saponification value. The saponification value of camelina oil was reported as 193.3 (mg KOH/g). The acid value of camelina oil was found to be 3.2 (mg KOH/g), corresponding to a free fatty acid (FFA) level of 1.58%, which is much lower than the upper limit of FFA content (3 wt%) in the oil for transesterification [21]. The camelina sativa oil consisting of 98.3% triglycerides acids was transesterificated with supercritical alcohols for biodiesel production. The viscosity at 40 °C of camelina sativa oil was determined to be 14.05–15.10 mm^2/s, and the pour point was −23 to −20 °C, respectively [32].