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Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor

Camila da Silva [a,b,*], Fernanda de Castilhos [c,d], J. Vladimir Oliveira [d], Lucio Cardozo Filho [b]

[a] Department of Technology, Maringá State University, (UEM), CEP: 87506-370, Umuarama, Brazil
[b] Department of Chemical Engineering, Maringa State University, (UEM). Av. Colombo 5790, Maringa, PR, 87020-900, Brazil
[c] Department of Chemical Engineering, Paraná Federal University (UFPR), Polytechnic Center (DTQ/ST/UFPR), Jardim das Américas, Curitiba, PR, 82530-990, Brazil
[d] Department of Food Engineering, URI, Campus de Erechim, Av. Sete de Setembro, 1621, Erechim, RS, 99700-000, Brazil

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ABSTRACT

This work investigates the production of fatty acid ethyl esters (FAEEs) from the transesterification of soybean oil in supercritical ethanol in a continuous catalyst-free process. Experiments were performed in a microtube reactor in the temperature range of 523 K to 598 K, from 10 MPa to 20 MPa, varying the oil to ethanol molar ratio from 1:10 to 1:40, and evaluating the effects of addition of carbon dioxide as co-solvent. Results showed that ethyl esters yield obtained in the microtube reactor (inner diameter 0.76 mm) were higher than those obtained in a tubular reactor (inner diameter 3.2 mm) possibly due to improved mass-transfer conditions attained inside the microtube reactor. Non-negligible reaction yields (70 wt.%) were achieved along with low total decomposition of fatty acids (<5.0 wt.%). It is shown that the use of carbon dioxide as co-solvent in the proposed microtube reactor did not significantly affect the ethyl esters yield within the experimental variable ranges investigated.

1. Introduction

The merits of biodiesel (fatty acid ethyl or methyl esters) obtained from vegetable oils or animal fats as an alternative to mineral diesel comprise a non-toxic, biodegradable, domestically produced and renewable source is well documented in the literature [1–4]. Because of the well-known environmental and economical benefits, biodiesel fuel may be expected as a good alternative to petroleum-based fuel.

Transesterification, among other processes used for biodiesel production, has been the most common way to produce biodiesel [1,2]. Conventionally, transesterification can be performed using alkaline, acid, enzyme catalysts or heterogeneous chemical catalysts [1,2,5–7].

Recently, a free-catalyst technique for the transesterification of vegetable oils using an alcohol at supercritical conditions has been proposed as an alternative method for biodiesel production [8–16]. According to the current literature, catalyst-free alcoholysis reactions at high temperature and pressure conditions provide improved phase solubility, decrease mass-transfer limitations, afford higher reaction rates and make easier separation and purification steps of the products. Besides, it has been shown that the so-called supercritical method is more tolerant to the presence of water and free fatty acids than the conventional alkali-catalyzed technique, and hence more tolerant to various types of vegetable oils, even for fried and waste oils [17–19]. Thus, the supercritical method appears to be attractive for application in continuous mode, which is the primary importance to assure a competitive cost to biodiesel fuel [20–24].

However, supercritical method requires high molar ratio of alcohol to oil and high temperature and pressure conditions for the reaction to present satisfactory yield levels, leading to high processing costs and causing in many cases the degradation of the fatty acids esters formed [25], hence decreasing the reaction yield [20–22,24]. Attempts to reduce the expected high operating cost and product degradation have been made through the addition of co-solvents [26–30], two-step process with removal of glycerol generated in the first step [31] and adopting a two-step process comprising hydrolysis of triglycerides in subcritical water and subsequent esterification of fatty acids [20,21].

Another approach suitable for the biodiesel production in supercritical conditions is the use of microreactor systems operating in continuous mode. Microreactor systems designed for continuous production have been studied in recent years for the transesterification of vegetable oils [32–36]. In the microreactor system, mass and heat transfer could be greatly intensified due to its small space with a large surface area-to-volume ratio [34], providing high process yields in low reaction times [33], that can in supercritical transesterification prevent the decomposition of fatty acids and decrease the operating conditions. However, studies available in the open literature refer to base-catalyzed alcoholysis reactions conducted at low pressure, with no reports found on the use of microreactors for the transesterification reaction at sub- and supercritical alcohol conditions.

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* Corresponding author. Department of Technology, Maringa State University, (UEM). Av. Angelo Moreira da Fonseca, Umuarama, PR, 87506-370, Brazil. Tel.: +55 44 36219339; fax: +55 44 36219300.
E-mail address: camiladasilva.eq@gmail.com (C. da Silva).

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In this sense, the main objective of the present work is to investigate the continuous transesterification of soybean oil under supercritical ethanol conditions in a microtube reactor. For this purpose it was assessed the effects of temperature in the range of 523 K to 598 K, pressure from 10 MPa to 20 MPa, oil to ethanol molar ratio from 1:10 to 1:40 and the addition of carbon dioxide as co-solvent for CO_2 to ethanol molar ratio ranging from 1:5 to 1:10.

2. Materials and methods

2.1. Materials

Commercial refined soybean oil (Soya) and ethanol (Merck 99.9%) were used as substrates without further treatment and carbon dioxide as co-solvent (White Martins, 99%). Other solvents, standards and reagents used in the derivatization step required for the analysis were supplied by Sigma-Aldrich. Chemical composition for the soybean oil used in this work is reported elsewhere [37]. The acid value (mg KOH/g) and water content (wt.%, Karl Fischer titration method, DL 50, Mettler-Toledo) were determined to be approximately 0.2 and 0.04, respectively.

2.2. Apparatus and experimental procedure

The experimental reaction system used in this work, schematically presented in Fig. 1, is similar to that used previously by Silva et al. [24], with the exception of the modification for carbon dioxide addition. Transesterification reactions were carried out in duplicate using a microtube reactor with a capacity of 36.5 mL made of stainless steel tubing (316 L 1/16 in. OD internal diameter 0.76 mm HIP). The substrates, ethanol and oil, were placed in a closed erlenmeyer and mixed by means of a mechanical stirring device and then were fed into the reaction system by a high-pressure liquid pump (Acuflow). Co-solvent (carbon dioxide) was added to the system at a pre-established flow rate using a syringe pump (Isco, model 500D). The microtube reactor was placed in a furnace with controlled temperature and monitored by two thermocouples directly connected at the inlet and outlet of the reactor. With this arrangement, the reaction temperature was controlled with a precision better than 5 K.

The system pressure was controlled by a control loop composed by a pressure transducer (Smar, model A5), a PID controller (Novus, Model N1100) and an electropneumatic valve (Baumann™, model 51000). Though more complex definitions can be used for the evaluation of the time spent in the reactor (the residence time) [21,24], in this work the residence time was computed dividing the volume of the reactor (mL) by the flow rate of substrates (mL/min) set in the liquid pump.

Samples were collected periodically in a glass vial placed at the reactor outlet after reaching the steady state condition, i.e., after a reactor space–time had been elapsed at least three times. Preliminary tests were carried out for some experimental conditions, affording excellent reproducibility of the experimental apparatus [38]. Based on duplicate experiments, the overall experimental error was found to be less than 5% on FAEE yield.

2.3. Gas chromatography (GC) analysis of fatty acid ethyl esters (FAEEs)

Samples were first submitted to ethanol evaporation to constant weight in a vacuum oven (338 K, 0.05 MPa) and then diluted with 2 mL of ethanol and 8 mL of n-heptane. Afterwards, a little amount was transferred to a 1 mL flask in order to obtain a concentration of 1000 ppm and then it was added the internal standard at a concentration of 250 ppm using n-heptane as solvent. After that, 1 μL of solution was injected in triplicate in the gas chromatograph (Shimadzu GC-2010), equipped with FID, autoinjector AOC-20i and a capillary column (DBWAX, 30 m × 0.25 mm × 0.25 μm). Column temperature was programmed from 393 K, holding 2 min, heating to 453 K at 10 K/min, holding 3 min, and to 503 K at 5 K/min, holding 2 min. Helium was used as carrier gas, and the injection and detector temperatures were 523 K with split ratio: 1:50.

Compounds were quantified upon analysis following the standard UNE-EN 14103 [39] and FAEE yield was then calculated based on the content of ethyl esters in the analyzed sample and on the reaction stoichiometry.

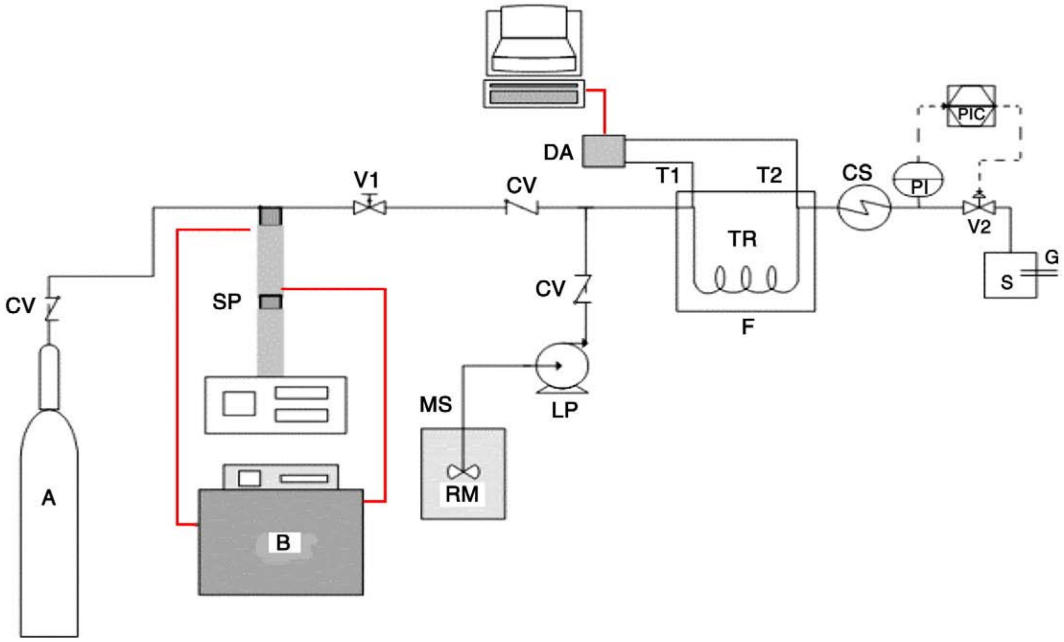

Fig. 1. Schematic diagram of the experimental apparatus. RM — reactional mixture; MS — mechanical stirring device; LP — high-pressure liquid pump; CV — check-valve; A — solvent reservoir; B — thermostatic baths; SP — syringe pump; F — furnace; TR — tubular reactor; T1 — temperature indicator at the reactor inlet; T2 — temperature indicator at the reactor outlet; DA — data acquisition system; CS — cooling system; V1 — feed valve; PI — pressure indicator; PIC — controller; V2 — pressure control valve; S — glass collector; G — gas output.