Fuel 227 (2018) 448–456

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Evaluation of the kinematic viscosity in biodiesel production with waste vegetable oil, ultrasonic irradiation and enzymatic catalysis: A comparative study in two-reactors

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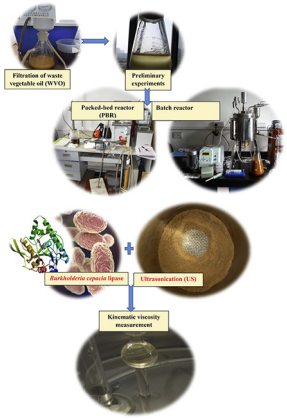
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Kinematic viscosity
Enzymatic catalysis
Esterification
Waste vegetable oil
Ultrasonic irradiation

ABSTRACT

In order to evaluate the biodiesel (BD) quality in a batch and a packed-bed reactor (PBR), a comparison was carried out in terms of the kinematic viscosity. Waste vegetable oil (WVO) and *Burkholderia cepacia* lipase were utilized as the main substrate and enzymatic catalyst, respectively. In the batch reactor, a kinematic viscosity of 36.75 $mm^2.s^{-1}$ at 20 °C was obtained in the first 2.5 min and 24.78 $mm^2.s^{-1}$ after 3 h with the application of ultrasound, without stirring. In the PBR, the lowest kinematic viscosity value was of 7.88 $mm^2.s^{-1}$ at 20 °C, and 5.83 $mm^2.s^{-1}$ at 40 °C, after 5 doses of 30 mL of methanol per round. The BD in both reactors was mainly produced by esterification of free fatty acids. The final mixture in the PBR met the requirement of kinematic viscosity of ASTM D6751-10, GB/T 19147-2003, and GB/T 265-1988 standards, respectively. Upon comparing the performance in both reactors, despite the limited BD yields, a common pattern of fast reduction in the kinematic viscosities was observed at the first reaction stages (approximately 70–80% reduction). Then flat-

Abbreviations: WVO, waste vegetable oil; US, ultrasonic; FAMEs, fatty acid methyl esters; PBR, packed-bed reactor; BCL, *Burkholderia cepacia* lipase; BD, biodiesel; SBO, soybean oil

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https://doi.org/10.1016/j.fuel.2018.04.119
Received 15 November 2017; Received in revised form 3 March 2018; Accepted 24 April 2018

shape values were measured in the last reaction stages. At applying further strategies in both reactors, higher BD concentrations could be obtained.

1. Introduction

The consumption of fossil fuels has resulted in many concerns related to its negative environmental effects [1,2]. Biodiesel (BD) of the second generation provides one environmentally sound alternative to fossil fuels because it can be produced from renewable resources [3]. Compared to petroleum diesel, its combustion generates fewer exhaust emissions [4], and as it comes from used or non-edible lipids such as waste vegetable oil (WVO) from sources including domestic use, restaurants, etc. It also does not generate a conflict with food. Instead, BD represents a more ecological and sustainable alternative to give an added value to food waste. The use of alkali catalysts, such as potassium hydroxide (KOH) and sodium hydroxide (NaOH), is one of the most conventional ways to produce BD, which is very common in industrial and commercial scale in many countries because of its low price and fast reactions [3]. However, the use of these catalysts implies the implementation of several processes, such as glycerol purification, pH neutralization, washing-drying of BD and wastewater treatment [5]. Moreover, the use of alkali catalysts is restricted to the acid number of the waste lipid source. In general, at very high acid number values it is better to use another kind of catalyst to avoid excessive soap formation and low BD yields. Therefore, enzyme-catalyzed transesterification could be a potential alternative for BD production.

Enzymes are proteins that act as catalysts. Most of the commercially available enzymes are extracted from fungi and bacteria. Enzyme-catalyzed transesterification has several benefits as compared to chemical-catalyzed transesterification including, complete conversion of feedstocks with high free fatty acids content together with no soap formation, no downstream processing required during the reaction, less energy consumption because the reaction can work under mild conditions, and the water content of feedstock does not influence the final product [6,7]. Heterogeneous enzyme-catalyzed transesterification using immobilized lipases (enzymes) on resins has been proven to enhance catalytic reactions more effectively than free lipases [8]. Transesterification process for BD production can be accomplished in only one-step when enzymatic or heterogeneous catalysis is applied as compared to chemical catalysis that required two-step transesterification to produce BD [9]. In addition, the use of complementary technologies can also increase the catalytic activity. For instance, ultrasonic (US) irradiation has proven to have positive effects. US technology uses energy in the way of sound; its waves vibrate beyond the human hearing limit (10–12 kHz). The US has three significant effects on reactions related to BD production: 1) it generates acoustic streaming mixing, 2) the variation of sonic pressures leads to a rapid movement of fluids and 3) occurrence of cavitation bubbles formed by liquid breakdown is caused by large negative pressure gradient applied on the liquid. The most important advantages of the US are shorter reaction times, lower alcohol to oil ratio, less energy consumption to achieve a similar effect without applying the US and a lower requirement of inorganic and enzymatic catalyst [10,11]. As the use of edible oil to produce BD creates socio-economic, legal and environmental conflicts, a convenient option is to use non-edible WVO feedstocks as a low-cost substrate for BD production.

Several experiments have been conducted using enzymatic catalysis with WVO under different conditions. For instance, Nie et al. [12] scaled-up the synthesis of fatty acid methyl esters (FAMEs) with the use of free *Candida* sp. as catalyst assisted by cyclodextrin at an agitation speed of 180 rpm and methanol was added 30 times in a 5000 L reactor. At these conditions, the yield of BD achieved 88%. Other study reported that 94.3% of FAMEs was obtained with immobilized Novozym®435 on a macroporous acrylic resin using waste cooking oil in a metallic packed-bed reactor (PBR) for a long-term set of reactions [13]. Huang et al. [14] demonstrated the effectiveness of US (28 kHz, 100 W power)-assisted immobilized *Candida antarctica* lipase-catalyzed transesterification of waste oil for the production of BD. In their conclusion, the transesterification reaction improved from 84.43% to 94.86%. In this study, *Burkholderia cepacia* lipase PS (BCLPS) was used as an enzyme catalyst in the transesterification of WVO for the production of BD. This enzyme has shown good thermal stability under a wide range of temperatures below 70 °C as well as a tolerance to high concentrations of methanol. In addition to the fact that this enzyme is capable to retain a good residual activity during several cycles of use, converting this lipase as a good candidate for scaled-up experiments to produce enzymatic BD. It was previously found that the specific transesterification activity of the free enzymes is 8348 U/g. However, when these enzymes were immobilized on NKA resin through the technique of physical adsorption, the specific transesterification activity reached 211733.3 U/g [8].

The industrial production of BD that uses WVO eventually implies the collection of this kind of oil from different sources, making more difficult to monitor its quality through its average molecular weight due to different kinds of cooking methods and temperatures. Alternatively, kinematic viscosity is one of the major fuel properties as prescribed in BD standards ASTM D6751 and EN 14214 as well as others [15]. Therefore, this study investigated the use of kinematic viscosity values as an indirect indicator of BD quality, especially this parameter depends on temperature only. Ellis et al. [16] successfully monitored the extent of transesterification reactions in a 300 L BD pilot plant by establishing a correlation between BD yield and kinematic viscosity using an acoustic wave solid-state viscometer, WVO as lipid source, methanol, KOH as a catalyst, and a reaction temperature of 60 °C. The authors reported that the measurements of kinematic viscosity provided valuable information in the production of BD along the reaction time. To the best of our knowledge, there have been no reports on the evolution of kinematic viscosity during enzymatic BD synthesis in a scaled-up context by BCLPS immobilized on KNA resin using WVO. Therefore, the objective of this study is to compare kinematic viscosity, as an indication of BD production, under the effects of US-assisted by BCLPS-catalyzed transesterification to produce BD from WVO in two reactors; a small PBR made of glass and the other is a batch reactor of 3 L capacity. Both reactors were designed in our laboratory in order to produce BD with immobilized enzymes as well as the application of US and emulsification simultaneously or separately (unpublished design of reactors). In the customized batch reactor, BCLPS was applied using US irradiation (without stirring/agitation of the emulsion) only to monitor the extent of reaction under the single effect of this technology. In PBR, recycling of the reaction mixture was performed (with water and glycerol extraction) in order to avoid complicated designs at installing several PBRs in series, installation of additional valves and pumps, etc. In each reactor, values of kinematic viscosity as the main parameter were measured under different reaction conditions. Furthermore, a correlation between kinematic viscosity and enzymatic BD was performed.

2. Materials and methods

2.1. Chemicals, reagents and equipments

The edible soybean oil (SBO) and waste vegetable oil (WVO) were obtained from Chinese local supermarkets at Wuhan and Zhongxingnonggu, respectively. Methanol (98%), ethanol (99%), n-hexane, sodium phosphate dibasic (Na_2HPO_4), sodium phosphate